

Development of Catalysts for the Ring-Opening Polymerization of Cyclic Esters and the Coordination-Insertion Polymerization of Olefins

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Dedication

This dissertation is dedicated to my parents; without you I would not be the person I am today. Your love and support have allowed me to believe in myself and my dreams. Your drive and dedication have inspired me to accomplish those dreams.

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Abstract

Over the past few decades, interest in the design and synthesis of tailorable polymeric materials has grown due to the well documented correlation between structure, property, and function. However, in order to obtain polymers with desired microstructures, well controlled synthetic methods are needed. Therefore, the continued investigation of homogeneous, single-site polymerization catalysts is important to gain a deeper understanding of how systematic modifications of polymerization conditions, ligand scaffold, metal center identity, cocatalyst or activator identity, etc. affect the catalytic activity, selectivity, and/or polymer topology obtained when using these catalysts for the polymerization of a variety of monomers. This dissertation will describe a portion of the advances and insights contributed by the Long Research Group towards furthering the fundamental understanding of catalyst structure for the polymerization of α -olefins and cyclic esters.

First our work within the field of redox-switchable catalysis (RSC) will be examined. RSC enables catalytic activity and/or selectivity to be oscillated based upon the oxidation-state of the ligand or active metal center. Unfortunately, though myriad redox-switchable catalysts have been developed for the ring-opening polymerization of cyclic esters, further fundamental structure-catalytic performance studies are needed to better ascertain how systematic changes in ligand structure impact catalytic activity and redox-switchability. Herein, we describe our studies designed to determine how the number of ligand-based redox-active moieties impact catalytic performance. More specifically, we compare symmetric catalysts bearing tetradentate [ONNO] ligands with two redox-active moieties to related asymmetric catalysts bearing tridentate [ONN] ligands featuring only a single redox-active moiety for the polymerization of L-lactide (L-LA). The results of these studies reveal that the number of redox-active moieties may not play a crucial role in the catalysts' switchability; however, the choice of metal center may dramatically influence catalyst activity, stability, and redox-switchability. Furthermore, we examine how ligand connectivity and conjugation affects catalytic activity, selectivity, and redox-switchability by comparing catalysts bearing salen-type ligands with two redox-active moieties to salan-type ligands with two redox-active moieties for the polymerization of L-LA and ϵ -caprolactone (CL). The results of these studies reveal that ligand connectivity and conjugation may both play a role in catalyst activity, selectivity, and redox-switchability.

Additionally, the ability to control the branching density of polyethylene (PE) has been of great interest within the field of olefin polymerization catalysis as a means by which polymer properties may be modulated. One method by which PE branching density may be control is through modulation of the catalysts via the inclusion of electron-withdrawing (EW) or electron-donating (ED) substituents to the ligand scaffold. However, while myriad of Pd- and Ni- centered α -diimine catalysts have been studied, a few key fundamental studies are still absent from the literature including a comprehensive examination of Ni-based α -diimine catalysts, as well as an examination of how placement of the substituent on the backbone versus placement on the *N*-aryl moieties affect polymer topology. Additionally, no method currently exists by which the polymer topology may be predicted based on an intrinsic characteristic of the catalyst-ligand combination without needing to perform exhaustive polymerization studies. Herein, we use a joint experimental and computational approach to demonstrate how placement of EW or ED substituents on the acenaphthene backbone, *N*-aryl moieties, or both the acenaphthene backbone and *N*-aryl moieties of Ni-based α -diimine catalyst affects PE branching density as compared the analogous unsubstituted catalyst. More specifically, we will show that inclusion of EW substituents results in decreased PE branching density, whereas inclusion of ED substituents results in little to no change in PE branching density. We will also show that as the placement and identity of the ligand substituents are varied, so too is the catalysts' reduction potential and

this relationship can be used to generate a calibration curve from which PE branching density may be predicted for other substituted Ni-based α -diimine catalysts without the need for extensive polymerization studies.

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Chapter 1 – Introduction to Redox Switchable Catalysis for the Ring-Opening Polymerization of Cyclic Esters

A portion of this chapter was originally published by Alicia M. Doerr, Justin M. Burroughs, Sean R. Gitter, Xuejin Yang, Andrew J. Boydston, and Brian K. Long in the peer-reviewed review article:

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I was responsible for surveying the literature and preparing the introduction, ring-opening polymerization, olefin polymerization, and summary sections of this review article, as well as formatting and editing all other sections. All portions of the review article adapted within this chapter were prepared by me. Justin M. Burroughs was responsible for surveying the literature and preparing the photochemical control sections (excluding ring-opening polymerization, olefin polymerization, and ring-opening metathesis polymerization section). Sean R. Gitter was responsible for surveying the literature and preparing the electrochemical control sections. Xuejin Yang was responsible for surveying the literature and preparing the ring-opening metathesis polymerization and mechanochemical control sections. Dr. Andrew J. Boydston and Dr. Brian K. Long advised this work and aided in the preparation of the review article.

1.1 Motivation

Interest in the design and synthesis of tailored polymeric materials has grown over the last few decades due to the well documented correlation between structure, property, and function.¹⁻⁵ In order to obtain polymers with desired microstructures, well controlled synthetic methods are crucial. Inspiration for these methods is often drawn from nature and the complexity seen within biological systems where protein sequences and structures are carefully controlled.⁶ Emulating the control and sophistication that is exhibited by biological systems to obtain highly defined polymer structures is one of the major goals within the synthetic polymer community.^{5,6} Introducing sophistication into synthetic polymeric materials is closely tied to the use of tailorable and tunable catalysts and initiator systems.⁷

Towards this goal, many advances and new developments have been made in the realm of controlled and living polymerization techniques.^{5, 8, 9} Early methods of controlled polymerization include the development of controlled free radical polymerization (CRP) methods,^{2,3,6,10} such as atom transfer radical polymerization (ATRP)^{4, 11} and reversible addition-fragmentation chain-transfer polymerization (RAFT),¹² as well as advances in polymerization methods like ionic polymerization,¹³ ring-opening polymerization (ROP),^{6, 14} chain walking coordination polymerization,^{6, 15} and ring-opening metathesis polymerization (ROMP).^{6, 16} These methods each provide a means by which the incorporation of functionalized monomers, monomer placement, and polymer architecture can be controlled to produce well-defined polymers.⁶ Furthermore, control over the formation of unique polymeric materials has been achieved via post polymerization modification using methods such as click chemistry,¹⁷ cross coupling reactions,¹⁸ or active esters;¹⁹ just to name a few.¹⁸ Despite the developments in functional group compatibility, molecular weight control, and stereocontrol, most polymerization techniques are unable to achieve the spatial or temporal control exhibited by many biological systems.

Endowing polymerizations with spatiotemporal control is highly intriguing and may open numerous avenues for the synthesis of bespoke polymeric materials. One method by which this control may be achieved is through the use of external stimuli to modulate the initiation and/or propagation steps of polymerization.⁷ These external stimuli can be used to elicit discrete, site-specific transformations that enable a system to toggle between distinct states.^{5, 20-24} When applied to various systems, external stimuli may be used to alter reactivity and selectivity

in situ, as well as enable modulation of polymer molecular weight, rate of monomer conversion, monomer sequence, dispersity, tacticity, and overall architecture, as well as many physical and mechanical properties.^{6, 7} Such stimuli include redox reagents, light, applied voltage or current, and mechanical force.^{5-7, 20, 23, 25-48} As well as the addition and/or removal of Cl,⁴⁹ metal cations,⁵⁰⁻⁶² borane⁶³⁻⁶⁸ to induce allosteric effects, CO₂⁶⁹⁻⁷⁵ and O₂⁷⁶⁻⁸⁰ as sources of gas-regulated systems, and acids and/or bases for pH regulated systems.⁸¹⁻⁸⁷ Herein, we will focus on the developments and advances in polymerizations modulated by redox-active catalysts for the ROP of cyclic esters that enable notable changes in polymerization kinetics, often creating an “on/off” type of behavior, and allowing polymeric materials with advanced architectures, such as block copolymers, to be accessed.

1.2 Redox-Switchable Catalysis

Redox-switchable catalysis (RSC) offers a means by which the activity and/or selectivity of a catalytic system may be modulated through oscillation of the oxidation state of either the active metal center or ligand scaffold.⁸⁸ Changes in the catalytic activity and selectivity of redox-active catalysts have been attributed to changes in the electron density at or around the active metal center as the system is switched reversibly between two stable oxidation states. The seminal example of RSC was reported in 1995 by Wrighton and colleagues who developed a diphosphinocobaltocene rhodium complex that was found to be approximately 16 times more active for the hydrogenation of cyclohexene in its reduced state than its oxidized counterpart (**Figure 1.1**).⁸⁹ The authors hypothesized that the greater activity observed for the reduced complex results from the active Rh-center being more electron-rich, which promotes the oxidative-addition of hydrogen as compared to the more electron-deficient Rh center of the oxidized complex. Following this seminal report, the field of RSC has expanded to include several polymerization methodologies such as ROP, coordination-insertion polymerization of olefins, ROMP, and CRP.^{5,}

20, 25, 26, 29, 41

1.3 Redox Switchable Ring-Opening Polymerization Catalysis

1.3.1 Ferrocene Containing Catalysts with Group IV Metal Centers

In 2006, Gibson and N. Long reported a salen catalyst bearing two redox-active ferrocenyl moieties and a Ti active metal center (**1**, **Scheme 1.1a**).⁹⁰ At 70 °C, catalyst **1** was significantly more active for the polymerization of *rac*-lactide (*rac*-LA) than its oxidized analogue (**1_{ox}**) ($k_{\text{red}}/k_{\text{ox}} \approx 30$). This change in catalytic activity could be reversibly switched via *in situ* addition of an oxidizing agent, silver triflate (AgOTf), which drastically slowed the rate of *rac*-LA polymerization (**Figure 1.2**). Upon subsequent addition of a reducing agent, decamethylferrocene (FeCp*₂), the polymerization activity resumed with a rate similar to that of **1** prior to oxidation ($k_{\text{app}} = 4.98 \times 10^{-6} \text{ s}^{-1}$, cf. $k_{\text{app}} = 4.73 \times 10^{-6} \text{ s}^{-1}$ before oxidation). Both **1** and **1_{ox}** produced atactic polylactide (PLA) with low dispersities ($\bar{D} \leq 1.20$), indicating that polymerization was well controlled. Catalyst **1** polymerizes LA via a coordination-insertion ROP mechanism (**Scheme 1.1b**) wherein the carbonyl oxygen of the monomer first coordinates to the active metal center (**II**). The carbonyl carbon of the monomer then undergoes nucleophilic attack by the alkoxide ligand of the catalyst to insert the carbonyl of the monomer between the active metal center and the alkoxide ligand (**III**). This is followed by isomerization to coordinate the ester oxygen to the metal center (**IV**), reformation of the carbonyl π -bond, and subsequent ring-opening via breaking of the C-O bond of the ester (**V**). It was hypothesized that the observed change in catalytic activity was due to modulation of the electron density around the active metal center upon oxidation and reduction though the exact mechanistic rationale was not well understood at the time.

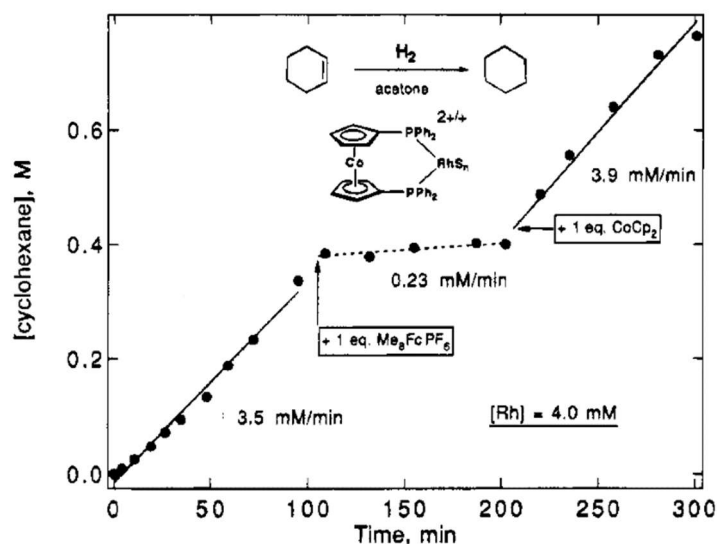


Figure 1.1 Plot of [cyclohexane] (M) vs. reaction time (min) for the hydrogenation of cyclohexene during an *in situ* redox switching experiment with a diphosphinocobaltocene rhodium complex. The reduced form of the catalyst is represented by the solid lines and the oxidized form is represented by the dotted line.⁸⁹ Reprinted with permission from J. Am. Chem. Soc. **1995**, *117* (12), 3617-3618. Copyright 1995 American Chemical Society.

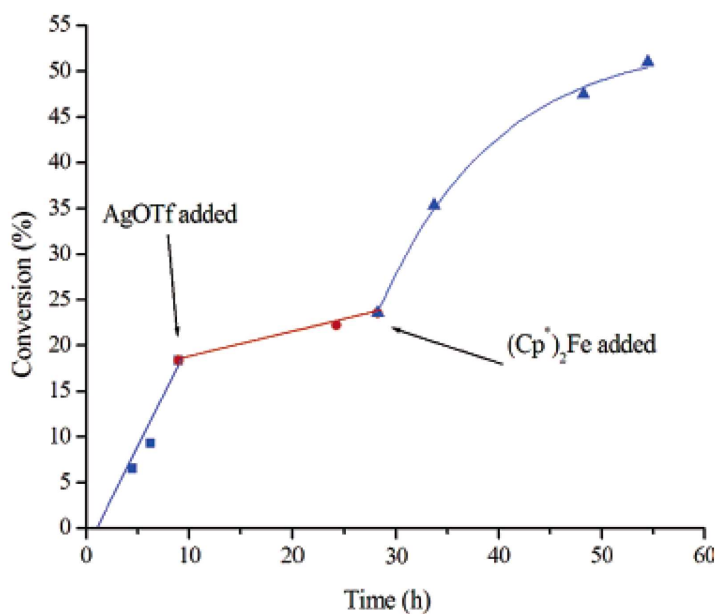
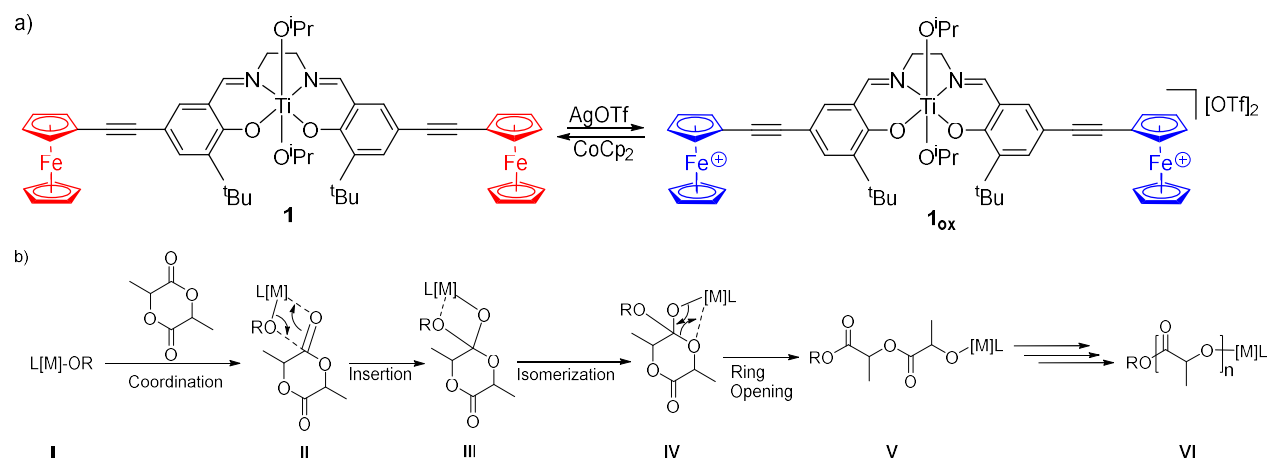


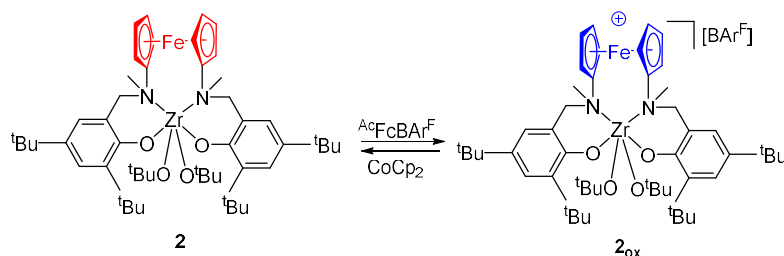
Figure 1.2 Plot of monomer conversion (%) vs. polymerization time (h) for the polymerization of *rac*-LA during the *in situ* redox switching of **1**.⁹⁰ Reprinted with permission from J. Am. Chem. Soc. **2006**, *128*, 7410-7411. Copyright 2006 American Chemical Society.

Scheme 1.1 (a) Redox-switching of Catalyst 1/1_{ox}; (b) General Mechanism of LA Polymerization by Coordination-Insertion ROP Catalysts



Following this seminal work, the groups of Diaconescu and B. Long each examined the redox-switching behavior of a variety of other group IV metal centered catalysts bearing redox-active ferrocenyl moieties about their ligand scaffolds.⁹¹⁻⁹⁸ While all of these studies showed differentiation in polymerization behavior upon changes in the oxidation state of the redox-active moieties, little was known about how these changes in oxidation state altered catalytic activity and selectivity until 2017 when Diaconescu and coworkers computationally studied the mechanistic details of the polymerization of LA with catalyst **2/2_{ox}** (**Scheme 1.2**).⁹⁴

Scheme 1.2 Redox-switching of Catalyst 2/2_{ox}



Because catalyst **2** is coordinatively saturated, some portion of the ligand is believed to dissociate to open a coordination site for monomer binding. It is hypothesized that this could occur through the dissociation of one or more nitrogen moieties as the strength of a Zr-O bond make dissociation of an alkoxide ligand unlikely. This is supported by Diaconescu's calculated structures that show dissociation of both nitrogen moieties from the metal center to facilitate coordination of the monomer (**Figure 1.3**).

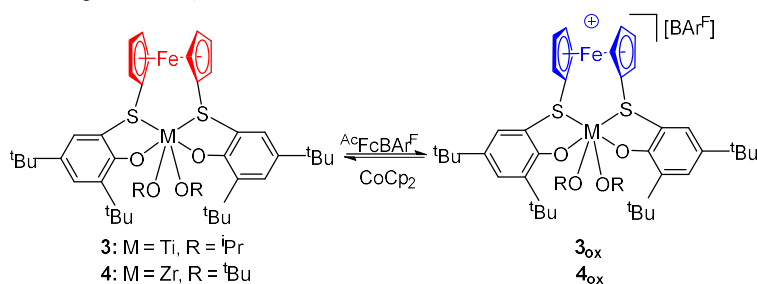
Once an open coordination site is generated, polymerization proceeds via coordination of monomer to the metal center followed by nucleophilic attack of the alkoxide ligand at the carbonyl carbon to generate intermediate **II-LA** (**Figure 1.4**). The oxygen of the ester then coordinates to the metal center followed by reformation of the carbonyl π -bond and breaking of the C-O bond of the ester to open the ring and form intermediate **III-LA**. This intermediate rearranges so that the carbonyl oxygen of the newly inserted LA is chelated to the metal center to form a relatively more stable five membered metallocycle intermediate **IV-LA**. In order for insertion of another LA

monomer to occur, the carbonyl must then dissociate to form intermediate **V-LA**. For catalyst **2**, the most stable intermediate for the first insertion of LA was shown to be **V^{red}-LA**, and the initiation step is energetically favored by 8.9 kcal/mol (**Figure 1.4**, top). Following initiation, propagation is also expected to be energetically favored as the enthalpy of polymerization of LA is reported to be about -5.5 kcal/mol,⁹⁹ leading to a further decrease in energy and therefore an active polymerization catalyst, which agrees well with experimental observations.

In contrast, oxidized catalyst **2_{ox}** features a ferrocenium moiety that decreases electron-density at the metal center and results in an increase in its electrophilicity, ultimately strengthening the coordination between the carbonyl group and Zr. Due to the strengthening of the coordination between the carbonyl and the metal center of catalyst **2_{ox}**, all intermediates and transition states of initiation were calculated to be lower in energy (**Figure 1.4**, middle) than the analogous intermediates and transition states of initiation with reduced catalyst **2** (**Figure 1.4**, top). However, chelated intermediate **IV^{ox}-LA** was dramatically lowered becoming the thermodynamically favored product of initiation, and therefore the theoretical catalyst resting state, which is believed to hinder further polymerization. Moreover, the calculations revealed that dissociation of the carbonyl group to form intermediate **V^{ox}-LA**, which would allow for further monomer coordination, was less stable than **IV^{ox}-LA** by 7.1 kcal/mol and the overall energy of propagation for **2_{ox}** was found to increase by 17.6 kcal/mol. This makes propagation thermodynamically unfavorable and results in **2_{ox}** being an inactive polymerization catalyst which agrees well with what was experimentally observed (**Figure 1.4**, bottom).

The redox-switchable polymerization behavior of group IV centered ROP catalysts have also been examined for a variety of other cyclic ester and ether type monomers including ϵ -caprolactone (CL) and cyclohexane oxide (CHO).⁹²⁻⁹⁷ For example, Diaconescu and colleagues studied the effect that the metal center identity had on catalytic activity for the ROP of both L-LA and CL via development of a Ti-centered thiolan catalyst (**3**), as well as, the Zr-centered analogue, **4** (**Scheme 1.3**).⁹⁵ Both catalysts **3** and **4** were observed to be more active for the ROP of L-LA than their oxidized forms, **3_{ox}** and **4_{ox}**. However, when comparing the two catalysts for the ROP of CL, opposite differentiations in activity were observed with **4** being more active than **4_{ox}**, whereas **3_{ox}** was more active than **3**.

Scheme 1.3 Redox-switching of Catalysts 3/3_{ox} and 4/4_{ox}



To investigate the differences in monomer selectivity observed between **3** and **4** for the ROP of CL, Diaconescu, Luo, and colleagues studied the mechanistic details of polymerization using DFT calculations.⁹⁶ The calculated overall activation energy barrier for **3_{ox}** was 32.7 kcal/mol; however, the overall activation energy barrier for reduced catalyst **3** was 38.2 kcal/mol, resulting in the reduced catalyst species being less active for the ROP of CL as compared to the oxidized catalyst, which is consistent with experimental results.^{95,96} This difference in overall activation energy was believed to be due to the increased electrophilicity of the Ti-center after catalyst oxidation,

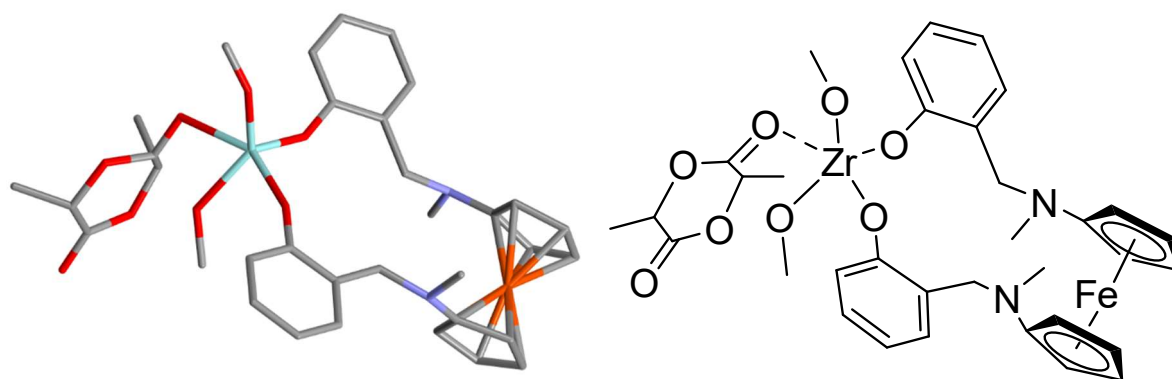


Figure 1.3 Calculated structure for the coordination of LA to catalyst **2**.⁹⁴ Adapted from *Organometallics* **2017**, *36*, 4451-4457. Copyright 2017 American Chemical Society.

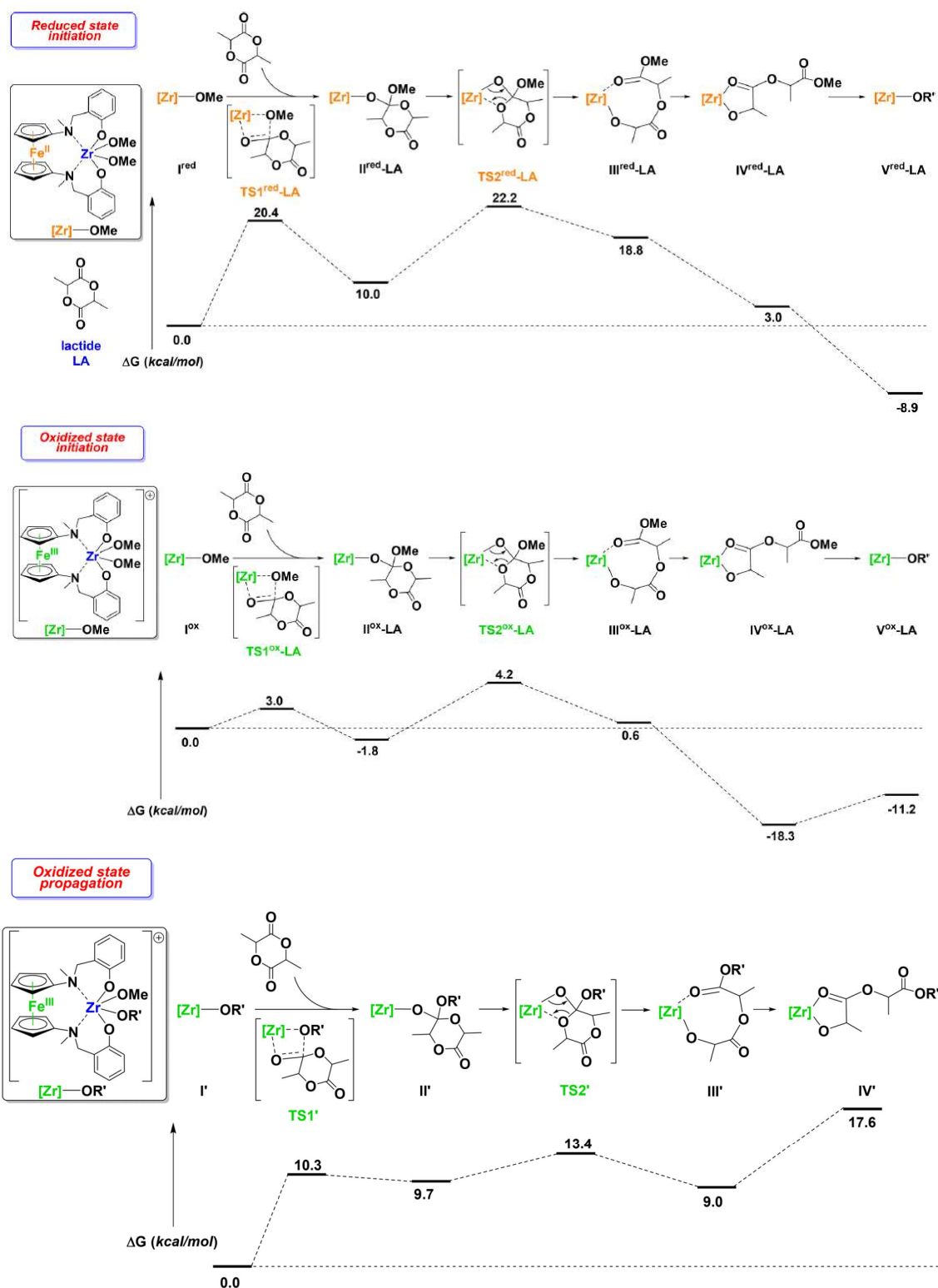
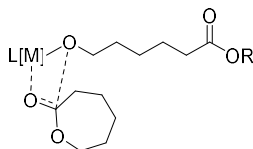


Figure 1.4 Potential energy surfaces for the ROP of LA by catalyst **2** (top) and **2_{ox}** (initiation, middle; propagation, bottom).⁹⁴ Reprinted with permission from *Organometallics* **2017**, *36*, 4451-4457. Copyright 2017 American Chemical Society.

which results in a stronger interaction between the coordinating monomer and Ti-center of **3_{ox}** as compared to **3** (-26.6 vs -20.2 kcal/mol), thereby facilitating monomer coordination and promoting propagation. Conversely, the polymerization of CL using **4** and **4_{ox}** exhibited overall activation energy barriers of 25.1 and 28.7 kcal/mol, respectively, resulting in the reduced complex being more active than the oxidized complex. This difference in activity is hypothesized to be due to the increased electrophilicity of the Zr-center after catalyst oxidation which strengthens coordination of the monomer carbonyl to the Zr-center as well as weakens the nucleophilicity of the alkoxide ligand of **4_{ox}**, as compared to **4**. Both of these changes result in the coordinated monomer intermediate shown in **Scheme 1.4** being the theoretical catalyst resting state and hindering further polymerization. Furthermore, it is hypothesized that the overall activity for the polymerization of CL with Zr- based catalyst **4** is greater than that of Ti-based catalyst **3** due to the higher effective nuclear charge and greater electrophilicity of Zr than Ti (Mulliken charge = 1.44 vs. 1.14, respectively).

Scheme 1.4 Coordinated Monomer Intermediate and Theoretical Catalyst Resting State Formed During the Polymerization of CL with **4_{ox}**



1.3.2 Ferrocene Containing Catalysts with Non-Group IV Metal Centers

Ferrocene containing ligand scaffolds have also been extended to the development of non-group IV-based redox-switchable ROP catalysts.¹⁰⁰⁻¹⁰³ In 2011, the Diaconescu group reported two phosfen complexes with either a yttrium (**5**) or indium (**6**) active metal center for the polymerization of L-LA (**Scheme 1.5**).¹⁰⁰ When *in situ* switching trials were performed using catalyst **5**, 24% monomer conversion was achieved in 1 h at 70 °C. Upon oxidation with ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate (FcBAr^F) to generate **5_{ox}**, the polymerization activity halted. When the complex was subsequently reduced with CoCp₂, the polymerization resumed with a rate similar to that observed prior to oxidation ($k_{app} = 0.3424 \text{ h}^{-1}$, cf. $k_{app} = 0.3733 \text{ h}^{-1}$ before oxidation) (**Figure 1.5**). Similar trends were also observed when **5** was used for the ROP of TMC. On the other hand, when **6** was tested for the ROP of TMC, the opposite trend was observed with the oxidized species, **6_{ox}**, being more active than the reduced species, **6**. These results indicated that the change in reactivity observed during oxidation and reduction of the redox-active ferrocenyl moiety is metal center dependent. Based on DFT calculations, it was hypothesized that these differences in catalytic activity upon oxidation of the ferrocenyl moiety are not only due to changes in the electrophilicity of the active metal center, but also to changes in the activation energies of the migration and/or ring-opening steps.

In addition to ferrocene containing ligand scaffolds bearing yttrium and indium centers, catalysts with La¹⁰¹ and Al^{102, 103} metal centers have also been investigated for the polymerization of a variety of cyclic ester and ether monomers. For example, the simplicity of synthesizing and easy control typically exhibited by Al-centered ROP catalysts makes them good complexes to use to investigate the polymerization mechanism of these redox switchable systems. Therefore, Diaconescu and colleagues developed an Al-centered thiolfan catalyst, **7** (**Scheme 1.6**), for the ROP of multiple cyclic ester and ether type monomers including L-LA and CL.¹⁰³ For the polymerization of L-LA,

Scheme 1.5 Redox Switching of Catalysts $5/5_{ox}$ and $6/6_{ox}$

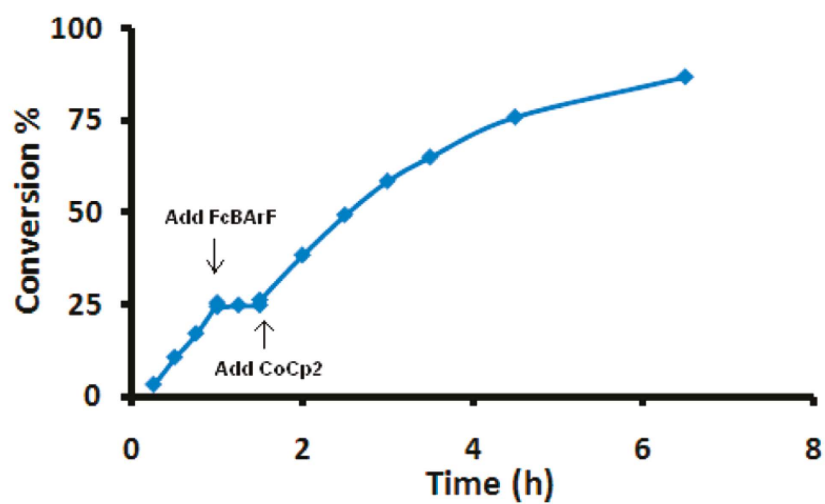
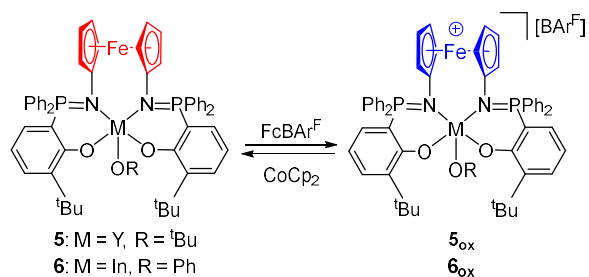
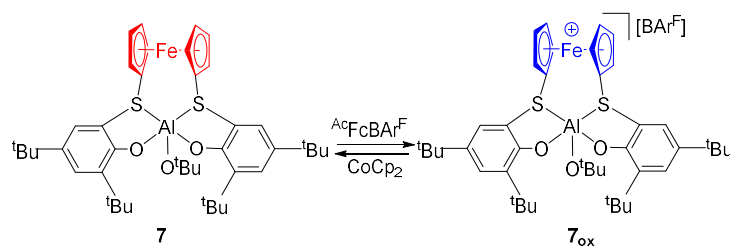


Figure 1.5 Plot of monomer conversion (%) vs. polymerization time (h) for the polymerization of L-LA during the *in situ* redox switching of **5**.¹⁰⁰ Reprinted with permission from J. Am. Chem. Soc. **2011**, *133*, 9278-9281. Copyright 2011 American Chemistry Society.

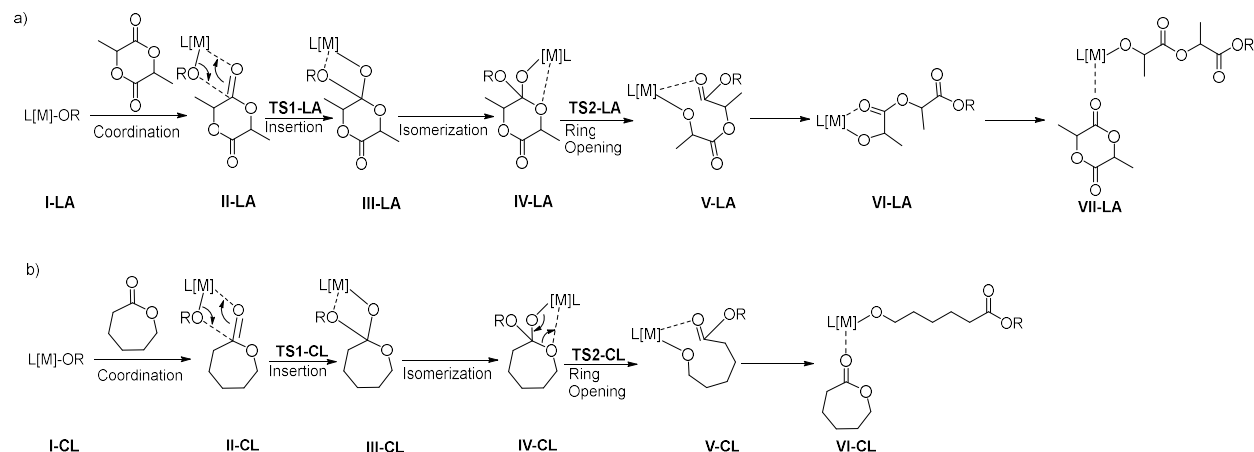
7 reached 88% monomer conversion in 24 h at 70 °C, whereas the oxidized species, **7_{ox}**, gave < 5% monomer conversion during the same time period at 100 °C. Alternatively, when tested for the polymerization of CL, catalysts **7** and **7_{ox}** were both found to be highly active. In order to better understand these differences in polymerization behavior DFT calculations were carried out to investigate the mechanistic details of initiation and propagation during the ROP of each monomer for both **7** and **7_{ox}**.¹⁰³ Through these computational results, they were able to deduce the rate determining step (RDS) for the polymerization and examine changes in polymerization activity observed experimentally.

Scheme 1.6 Redox Switching of Catalysts **7**/**7_{ox}**



Based on computational results, it was hypothesized that the differences in monomer selectivity observed were due to changes in the RDS of the polymerization (**Scheme 1.7**). It was shown that the RDS for the polymerization of LA is the ring-opening step (**TS2-LA**, **Scheme 1.7a**) while the RDS for the polymerization of CL is the nucleophilic attack by the alkoxide ligand (**TS1-CL**, **Scheme 1.7b**). This difference in RDS is believed to be due to the higher ring strain of CL as compared to LA ($\Delta H_P = -29$ vs. -23 kJ/mol, respectively) making the ring-opening of CL energetically more favorable than that of LA.⁹⁹ It should also be noted that after insertion of the first CL monomer, chelation of the carbonyl to the metal center forms a nine membered metallocycle intermediate (**V-CL**) which is less stable than the carbonyl chelated five membered metallocycle intermediate formed during the polymerization of LA (**VI-LA**). In order for subsequent monomer coordination to occur, the chelated carbonyl in intermediates **V-CL** and **VI-LA** needs to dissociate. Therefore, formation of the less stable nine membered metallocycle intermediate (**V-CL**) is believed to result in the faster overall rate of polymerization observed for CL, as compared to LA, as the energy barrier for dissociation of the carbonyl is lower.

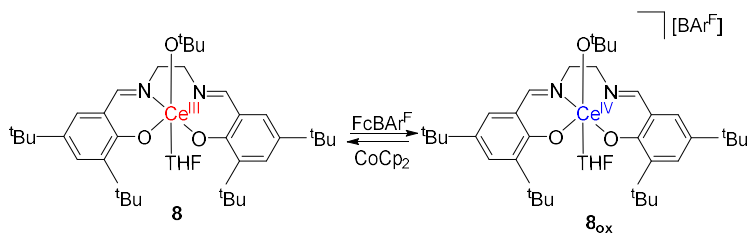
Scheme 1.7 Mechanism for the ROP of (a) LA and (b) CL



1.3.3 Metal Centered Redox-Active Catalysts

Lastly, researchers have also investigated the development of redox-switchable catalysts wherein the active metal center itself can undergo oxidation and reduction instead of including a redox-active moiety on the ligand scaffold.¹⁰⁴⁻¹⁰⁹ This was first reported in 2011 by Diaconescu, Cantat, and colleagues using a salen-type ligand and a cerium active metal center (**8**) (Scheme 1.8).¹⁰⁶ When implemented for the ROP of L-LA at ambient temperatures, the native Ce(III) complex (**8**) was polymerization active, whereas the oxidized Ce(IV) complex (**8_{ox}**) was much less active. During an *in situ* redox-switching experiment, catalyst **8** reached 29% monomer conversion in 15 min, then upon oxidation with FcBAR^F the polymerization activity was seen to halt. After 20 min, CoCp₂ was subsequently added, resulting in regeneration of **8** and reactivation of polymerization activity with a rate roughly the same as prior to oxidation (before: $k_{app} = 1.96 \times 10^{-2}$; after: $k_{app} = 1.73 \times 10^{-2}$). *In situ* redox switching was conducted three times successively without any observable decrease in polymerization activity, indicating that the redox switch between **8** and **8_{ox}** was reversible. It was hypothesized that the difference in activity observed is due to either 1) the larger ionic radius of Ce(III) which favors the coordination of the incoming monomer, or 2) the increased electrophilicity of Ce(IV), which decreases the nucleophilicity of the alkoxide ligand. To investigate the influence of the electronic effect on the polymerization behavior of **8** and **8_{ox}**, DFT calculations were used to examine key intermediates and transition states. It was found that the transition states and intermediates associated with the ring-opening of the monomer induced by migration of the alkoxide ligand were about 5 kcal/mol higher in energy for **8_{ox}** than for **8**. This supported the authors' hypothesis that the decreased nucleophilicity of the alkoxide ligand in **8_{ox}** contributed to the lower polymerization activity observed experimentally.

Scheme 1.8 Redox Switching of Catalysts **8/**8_{ox}****



In addition to Ce, Fe has also been explored for the development of these metal centered redox-active catalysts.^{105, 108} For example, the Byers groups examined the redox-switching behavior of an Fe-centered bis(imino)pyridine catalyst (**9**) (Scheme 1.9) for the polymerization of *rac*-LA.¹⁰⁵ In the presence of an alcohol initiator, **9** was observed to be more active for the ROP of *rac*-LA than the oxidized species, **9_{ox}**. During an *in situ* switching experiment, **9** reached 25% monomer conversion in 40 min followed by halting of polymerization activity upon oxidation with ferrocene hexafluorophosphate (FcPF₆) (Figure 1.6). Subsequent reduction with CoCp₂ resulted in the resumption of polymerization activity with a rate similar to that seen prior to oxidation ($k_{obs} = 2.2 \times 10^{-4} \text{ s}^{-1}$, cf. $k_{obs} = 1.5 \times 10^{-4} \text{ s}^{-1}$ before oxidation). They also showed that the catalyst system was able to undergo multiple consecutive *in situ* switches with little to no change in polymerization activity, polymer molecular weight, or dispersity.

Scheme 1.9 Redox Switching of Catalysts $9/9_{ox}$

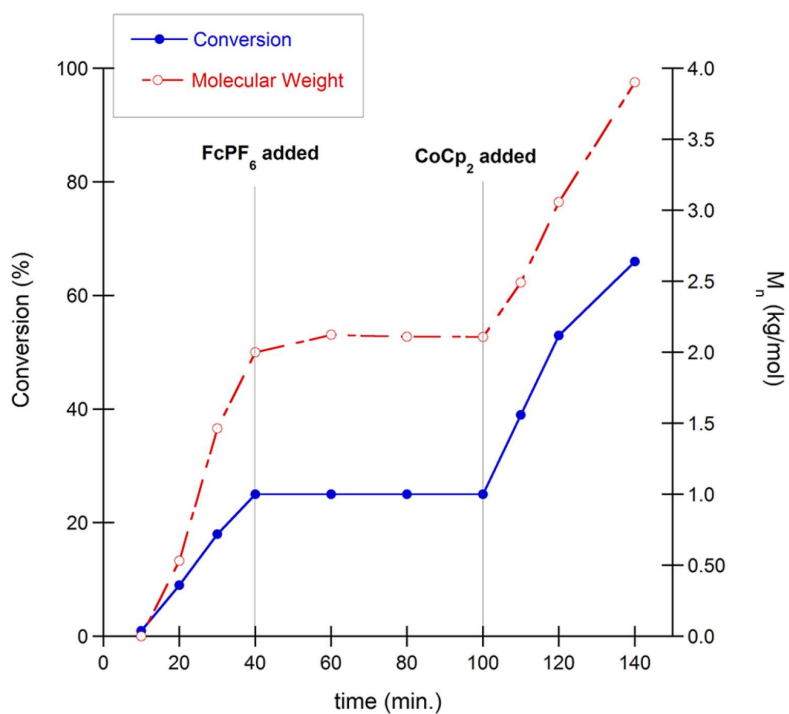
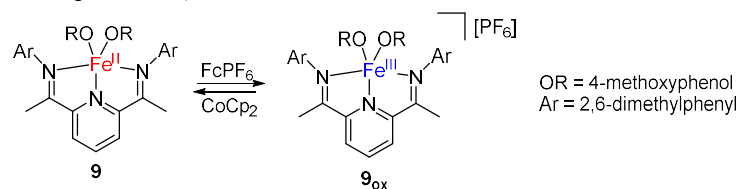
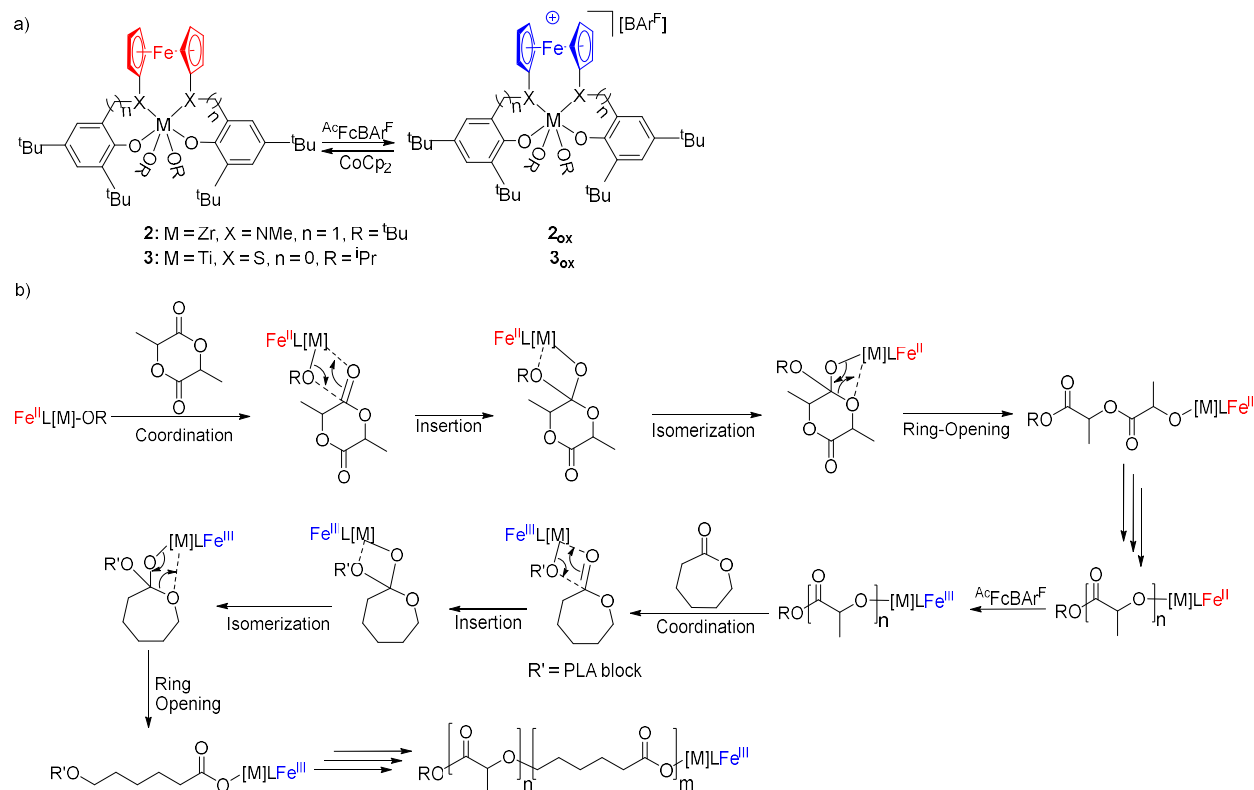


Figure 1.6 Plot of monomer conversion (%) vs. polymerization time (min) for the polymerization of *rac*-LA during the *in situ* redox switching of **9**.¹⁰⁵ Reprinted with permission from J. Am. Chem. Soc. **2013**, *135*, 16553-16560. Copyright 2013 American Chemistry Society.

1.4 Potential Application of Redox-Switchable Catalysts

The differentiation in catalytic activity and selectivity exhibited by redox-switchable catalysts offers a new synthetic methodology by which advanced polymer architectures, such as block copolymers, may be obtained. Diaconescu and coworkers were the first to investigate the potential of RSC for the formation of block copolymers using catalysts **2** and **3** (Scheme 1.10a) for the polymerizations of L-LA and CL.⁹² When the ROP of L-LA was conducted at 80-100 °C, both catalysts exhibited higher polymerization activities in the native state than in the oxidized state (Figure 1.7a). On the other hand, when tested for the ROP of CL at ambient temperatures, the orthogonal activity was demonstrated with the oxidized states being more active than the reduced states (Figure 1.7b). This orthogonal polymerization activity is believed to be due to the difference in the RDS for each monomer, as was previously discussed.¹⁰³

Scheme 1.10 (a) Redox-switching of Catalysts 2/2_{ox} and 3/3_{ox}. (b) Mechanism for the Redox-Switchable One-Pot Block Copolymerization of LA and CL with catalyst 3



Based on these results, a one-pot block copolymerization was attempted in which *in situ* oscillation of the catalyst's oxidation state resulted in modulation of monomer selectivity (Scheme 1.10b). Catalyst **3** reached 58% L-LA conversion in 36 h with little to no conversion of CL. Upon oxidation *in situ* with AcFcBARF to generate oxidized catalyst **3_{ox}**, CL conversion reached 18% with no additional polymerization of L-LA. Though the resultant block copolymers were poorly controlled, this seminal report showed the power of RSC for one-pot block copolymer formation. Block copolymer formation was also attempted with **2**. However, following *in situ* oxidation to form **2_{ox}**, no conversion of CL was observed, which was attributed to the strong coordination of L-LA to the Zr active metal center, ultimately preventing coordination of CL.

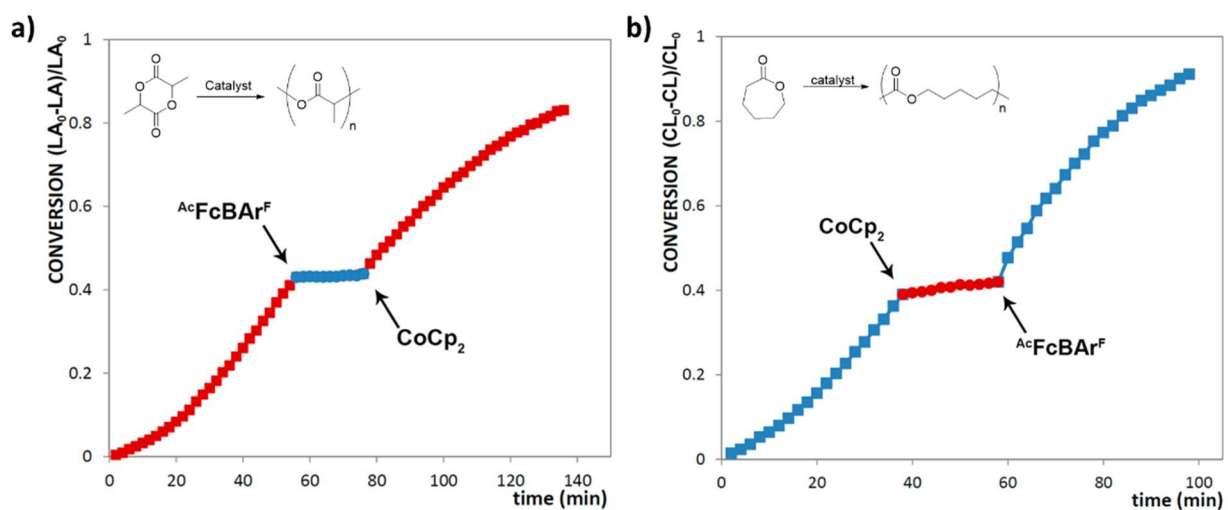


Figure 1.7 Plot of monomer conversion (%) vs. polymerization time (min) for the polymerization of (a) L-LA and (b) CL during the *in situ* redox-switching of **2**.⁹² Reprinted with permission from J. Am. Chem. Soc. **2014**, *136*, 11264-11267. Copyright 2014 American Chemical Society.

Following this seminal report, Diaconescu and coworkers expanded their comonomer library to include a variety of other cyclic esters and ethers, such as β -butyrolactone, δ -valerolactone, oxetane, trimethylene carbonate, propylene oxide, cyclohexene oxide (CHO), and styrene oxide.^{93-95, 97, 102, 103} During these studies, CHO was found to be a highly orthogonal partner to LA allowing the researchers to obtain di- and tri-block copolymers with well controlled block definition using multiple different catalysts.^{93, 95, 97, 102, 103} For example, reduced catalyst **2** was highly active towards the polymerization of L-LA, reaching 93% monomer conversion after 3 h at 100 °C, whereas no polymerization was observed after 24 h using the oxidized form, **2_{ox}**, under the same conditions.⁹³ In contrast, **2** exhibited no observable activity towards the ROP of CHO after 24 h at 100 °C, whereas **2_{ox}** reached 95% monomer conversion in only 1.5 h. Based in this these results, *in situ* redox-switching block copolymerizations were then conducted via sequential monomer addition leading to the formation of di- and triblock copolymers of varying compositions, depending on the initial catalyst oxidation state. For example, when starting from **2** PLA-PCHO-PLA triblock copolymers could be obtained, whereas when starting with **2_{ox}** PCHO-PLA-PCHO triblock copolymers were obtained.

The Byers Group has also shown that their previously studied Fe-centered bis(imino)pyridine catalyst **9** could be used for redox-switchable one-pot block copolymerizations.¹⁰⁴ In this study, CHO emerged as a highly active and orthogonal partner to LA with the oxidized species, **9_{ox}**, being more active for the ROP of CHO than the reduced species, **9**. During *in situ* redox-switching experiments, **9_{ox}** reached 40% monomer conversion in 50 min before being reduced with CoCp₂, halting of all polymerization activity. Upon subsequent oxidation with FcPF₆, the polymerization activity resumed with a rate similar to that observed prior to reduction ($k_{\text{obs}} = 1.23 \times 10^{-4} \text{ s}^{-1}$, cf. $k_{\text{obs}} = 2.54 \times 10^{-4} \text{ s}^{-1}$ before reduction). Based on these results, they were able to obtain both PLA-PCHO and PCHO-PLA block copolymers via one-pot *in situ* redox-switching copolymerizations, in which excellent definition between blocks was observed (e.g. 98% *rac*-LA conversion with no observable CHO conversion followed by 68% CHO conversion with no further conversion of *rac*-LA). It was hypothesized that the switch in chemoselectivity observed for **9** arises from the difference in electron density at the Fe-center (Fe^{II} vs. Fe^{III}). The polymerization of LA would benefit from nucleophilic activation of the alkoxides, which is characteristic of a more electron rich Fe^{II} center. Conversely, the polymerization of an epoxide (CHO) would benefit from electrophilic activation, which is characteristic of a more electron deficient Fe^{III} center.

The Byers group then used this orthogonal monomer reactivity between LA and epoxides to develop the first redox-triggered crosslinking network through the development of an epoxy-cyclic diester bifunctional monomer.¹⁰⁷ The cyclic diester portion of the monomer could be selectively polymerized by **9** to obtain an epoxide functionalized polyester with good control ($D = 1.4$). Upon oxidation with FcPF₆, to generate **9_{ox}** the epoxide side chains were selectively crosslinked to produce a polymer network that was insoluble in all solvents tested. The reverse activity was also exhibited through the polymerization of the epoxide moieties followed by catalyst reduction and crosslinking of the cyclic diester functionalities (**Figure 1.8**).

1.5 Research Objectives

Though multiple studies have provided proof-of-concept evidence that supports the ability of RSC to modulate polymerization activity *in situ*, further fundamental structure-catalytic performance studies are needed to better ascertain how systematic changes in ligand structure impact catalytic activity and redox-switchability. With further understanding of the fundamental structure-catalytic performance relationship of these catalysts, researchers will be able to better design redox-switchable ROP catalysts for the formation of tailored materials.

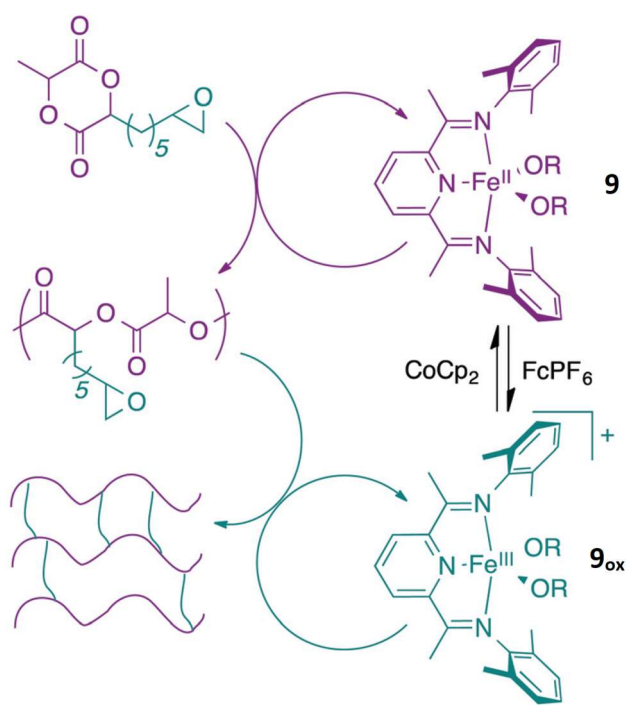


Figure 1.8 Polymerization of an epoxy-cyclic diester monomer with catalyst **9** and redox-triggered crosslinking (OR = *p*-methoxy phenoxide, Fc = ferrocenium, Cp = cyclopentadienyl).¹⁰⁷ Reprinted with permission from Polymer Chemistry **2016**, 7, 4675-4681. Copyright 2016 Royal Society of Chemistry.

In Chapters 2 and 3 we will investigate how the number of redox-active moieties on the ligand scaffold, ligand denticity, ligand connectivity, conjugation, and the identity of the active metal center affect catalytic activity, selectivity, and redox-switchability of [ONNO] and [ONN] group IV metal centered catalysts for the polymerization of L-LA and CL (**Figure 1.9**). The scope of these projects includes:

- I. Design and synthesis of redox-active [ONN]- and [ONNO]-type ligands
- II. Synthesis of redox-active catalysts with group IV active metal centers
- III. Characterization of all ligands (^1H and ^{13}C NMR spectroscopy and mass spectrometry) and catalysts (^1H and ^{13}C NMR spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction)
- IV. Polymerization studies of L-LA and CL and characterization of the resulting polymers using ^1H NMR spectroscopy and gel permeation chromatography (GPC)

In Chapter 2, the effect of the number of redox-active moieties, ligand denticity, and active metal center identity on catalytic activity and redox-switchability are investigated. In order to study the effects of these factors two tridentate [ONN] Schiff base-type group IV centered catalysts bearing one ferrocenyl moiety were tested for the polymerization of L-LA and compared to the results obtained for a tetradentate [ONNO] salen-type group IV centered catalyst bearing two ferrocenyl moieties. The synthesis and characterization of two Ti or Zr-centered catalysts as well as their polymerization behavior in both the reduced and oxidized states is discussed. Through comparison of these catalysts, it was shown that number of redox-active moieties and ligand denticity may have an impact on catalyst activity and stability but not on redox-switchability. Conversely, the metal center identity may play a role in catalyst activity, stability, and redox-switchability.

In Chapter 3, the effects that ligand connectivity, conjugation, and metal center identity have on catalytic activity, selectivity, and redox-switchability are investigated. These factors are examined through comparison of the polymerization behavior of [ONNO] salen-type (imine containing) catalysts with group IV metal centers bearing two ferrocenyl moieties to the behavior of related [ONNO] salan-type (amine containing) catalysts with group IV metal centers bearing two ferrocenyl moieties for the polymerization of L-LA and CL. The synthesis and characterization of these Ti- or Zr-centered catalysts are discussed as well as their L-LA and CL polymerization behavior in both the reduced and oxidized states. Through comparison of these catalysts, it was shown that ligand connectivity and conjugation may both play a role in catalyst activity, selectivity, and redox-switchability.

We will then transition to an introduction on the development of ethylene polymerization catalysts starting with heterogeneous complexes through the design of late transition metal non-metallocene catalysts (Chapter 4). Then in Chapter 5, will discuss our contributions to the study of Ni-based α -diimine catalysts, wherein we experimentally and computationally investigate how the placement and identity of electron-withdrawing (EW) and electron-donating (ED) substituents on the ligand scaffold affect topology of the polyethylene (PE) produced.

In Chapter 6, a summary of the dissertation work described within Chapters 1-5 will be provided as well as an outlook for the development of redox-active catalysts for the polymerization of α -olefins. Chapter 6 will also include some preliminary work for a proposed redox-switchable polymerization catalyst study. The references for all chapters will be presented after Chapter 6. Additionally, the data that is secondary to the project goals for Chapters 2-6 will be provided in Appendix A, including experimental procedures, representative NMR spectra, representative GPC traces, cyclic voltammograms, X-ray crystallography data, and DSC spectra.

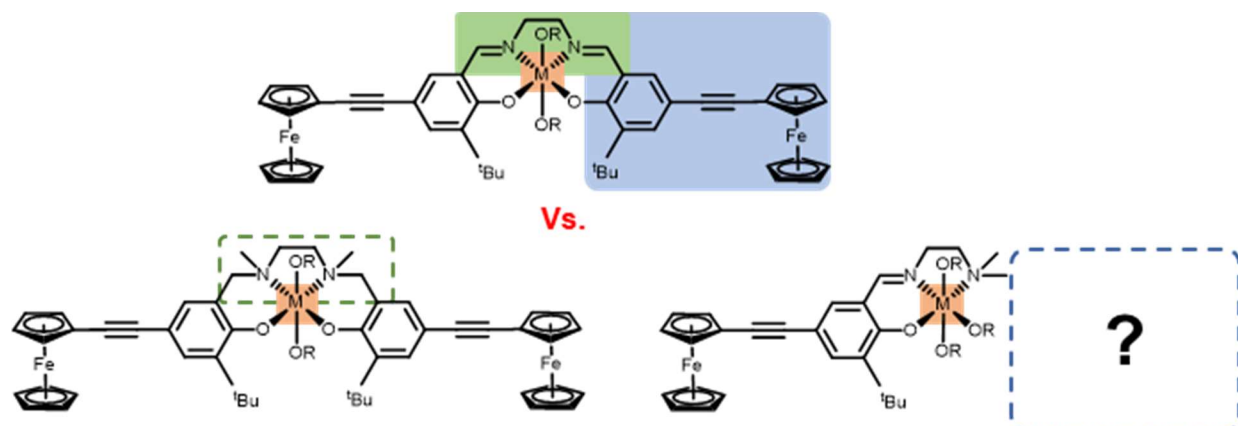


Figure 1.9 Overview of catalysts developed in Chapters 2 and 3 to study how the number of redox-active moieties on the ligand scaffold, ligand denticity, ligand connectivity, conjugation, and the identity of the active metal center effect catalytic ROP behavior of cyclic esters.

Chapter 2 – Redox-Switchable Ring-Opening Polymerization by Tridentate [ONN]-Type Titanium and Zirconium Catalysts

A version of this chapter was originally published by Alicia M. Doerr, Justin M. Burroughs, Nicholas M. Legaux, and Brian K. Long in the peer-reviewed manuscript:

Alicia M. Doerr, Justin M. Burroughs, Nicholas M. Legaux, Brian K. Long. “Redox-Switchable Ring-Opening Polymerization by Tridentate ONN-Type Titanium and Zirconium Catalysts.” *Catalysis Science & Technology*. **2020** 10, 6501-6510, DOI: 10.1039/D0CY00642D.

I performed the ligand and catalyst synthesis and characterization presented within this work. I also performed all polymerizations discussed, as well as writing most of the document. Justin Burroughs obtained and analyzed all X-ray crystallographic data provided and Nicholas Legaux assisted with ligand and catalyst synthesis. Dr. Brian Long advised this work.

2.1 Introduction

The consumer plastics market is dominated by synthetic, petroleum-based polymers such as PE and polypropylene (PP).¹¹⁰⁻¹¹² While these polymers exhibit exceptional thermal and mechanical properties, they also display a high degree of degradation resistance. This results in decomposition periods on the order of hundreds of years and contributes to the world’s vast accumulation of plastic waste.¹¹⁰⁻¹¹² Because of this issue, biodegradable alternatives to petroleum-derived plastics are highly sought after.^{111, 113}

One class of polymers that has shown particular promise as a biodegradable alternative are polyesters such as PLA and poly(ϵ -caprolactone) (PCL). These polyesters are commonly synthesized via ROP of their respective cyclic esters^{111, 114-117} using either transition metal-based species or organocatalysts.^{118, 119} Of these, transition metal-based catalysts have gained particular interest due to the degree of polymerization control and tunability they imbue.

A particularly intriguing class of transition metal-based catalysts for the ROP of cyclic esters are tetradentate [ONNO] salen-type catalysts.^{90, 106, 120-149} These catalysts have been extensively studied, wherein the electronic nature of the ligand was found to have a dramatic influence over the reactivity of the catalyst. As an example, Gibson and Long reported a library of Ti-salen complexes bearing either ED or EW pendant groups, and found that catalysts bearing more electron-rich ligands were up to three times faster for the ROP of rac-LA than catalysts bearing EW groups.¹²⁹ They then extended this study to include the development of the first redox-active ROP catalyst (**1**, **Figure 2.1**),⁹⁰ which showed that the reactivity of this catalyst could be oscillated between active and nearly dormant states ($k_{\text{red}}/k_{\text{ox}} \approx 30$) through the oxidation and reduction of the ligand’s ferrocenyl moiety. This ability to oscillate a catalyst’s activity and/or reactivity based upon redox state is now frequently referred to as RSC.

Interest in applying RSC to the ROP of cyclic esters has grown considerably in recent years. Numerous examples capitalize on the ability to modulate catalytic behavior through the use of added chemical oxidants and reductants, as well as other external stimuli.^{87, 88, 90, 92, 93, 95, 97, 100, 104, 106, 150, 151} In these studies, oxidation and/or reduction is believed to perturb the electronic nature of the catalyst’s active site, frequently resulting in altered rates of polymerization and/or monomer selectivity, which has enabled the synthesis of various block copolymers. For example, Diaconescu and colleagues used DFT calculations to show how electronic perturbations of redox-switchable catalysts affects LA polymerization activity (**Figure 1.4**).⁹⁴ They found that following insertion and ring-opening of the first monomer, the carbonyl oxygen of opened LA monomer chelates the metal center to form

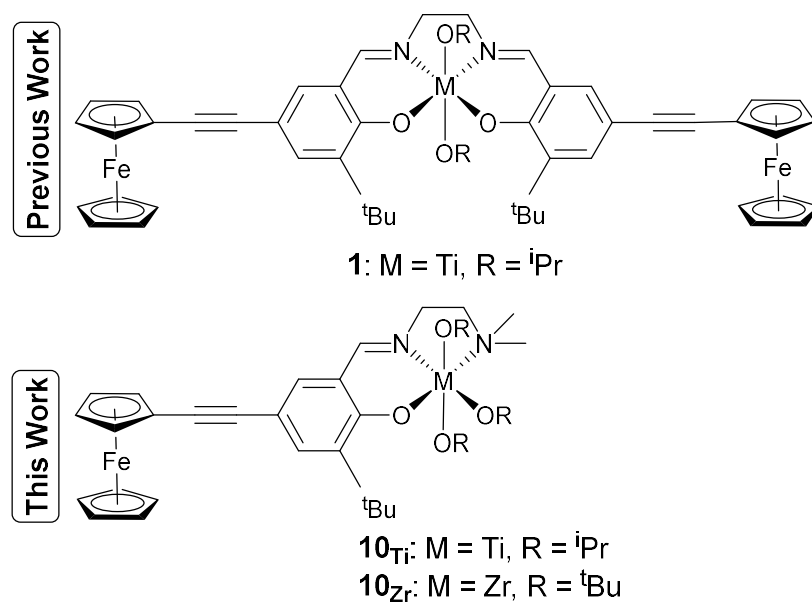


Figure 2.1 Symmetric tetradentate [ONNO] catalyst **1** as compared to asymmetric tridentate [ONN] catalysts **10_{Ti}** and **10_{Zr}**.

a five membered metallocycle intermediate (**IV^{red}-LA**, **Figure 1.4**, top), which must open in order to coordination subsequent LA monomers (**V^{red}-LA**). In the reduced ligand state, carbonyl dissociated complex **V^{red}-LA** is calculated to be the thermodynamically favored intermediate of initiation. Propagation is also expected to be energetically favored as the enthalpy of polymerization of LA is reported to be approximately -5.5 kcal/mol,⁹⁹ leading to a further decrease in energy and therefore an active polymerization catalyst. Conversely, upon catalyst oxidation, the electron-density at the active metal center is decreased relative to the native catalyst resulting in a strengthening of the coordination between the carbonyl of ring-opened LA and the metal center. This results in metallocycle intermediate **IV^{ox}-LA** (**Figure 1.4**, middle) becoming the thermodynamically favored product of initiation, and therefore the theoretical catalyst resting state, which hinders further polymerization. Moreover, calculations reveal that dissociation of the carbonyl group from the oxidized catalyst to allow for further monomer coordination is less favored thermodynamically, while the overall energy of propagation is also thermodynamically unfavorable resulting in an inactive polymerization catalyst (**Figure 1.4**, bottom).

Due to the differentiation in catalyst activity and selectivity exhibited upon modulation of catalyst oxidation state, redox-switchable catalysts offer a means by which advanced polymer architectures (e.g. block copolymers) may be obtained.^{92-95, 97, 102, 103} While multiple studies have provided proof-of-concept evidence supporting the ability of redox-switchable catalysts to be used for (multi)block copolymer synthesis, further fundamental structure-catalytic performance studies are still needed. This understanding will enable researchers to better design future generations of redox-switchable ROP catalysts for the formation of tailored materials.

Inspired by these works, we sought to better understand how ligand structure, namely the number of redox-active moieties, impacts catalytic activity and redox-switchability. Because the vast majority of transition metal-based redox-switchable catalysts developed for the ROP of cyclic esters have been symmetric in nature, such as prototypical catalyst **1**,^{90-93, 95, 100, 103, 105, 106, 108, 109} we sought to determine the efficacy of their closely related asymmetric, tridentate analogues **10_{Ti}** and **10_{Zr}**, which bear only a single ferrocenyl moiety (**Figure 2.1**).

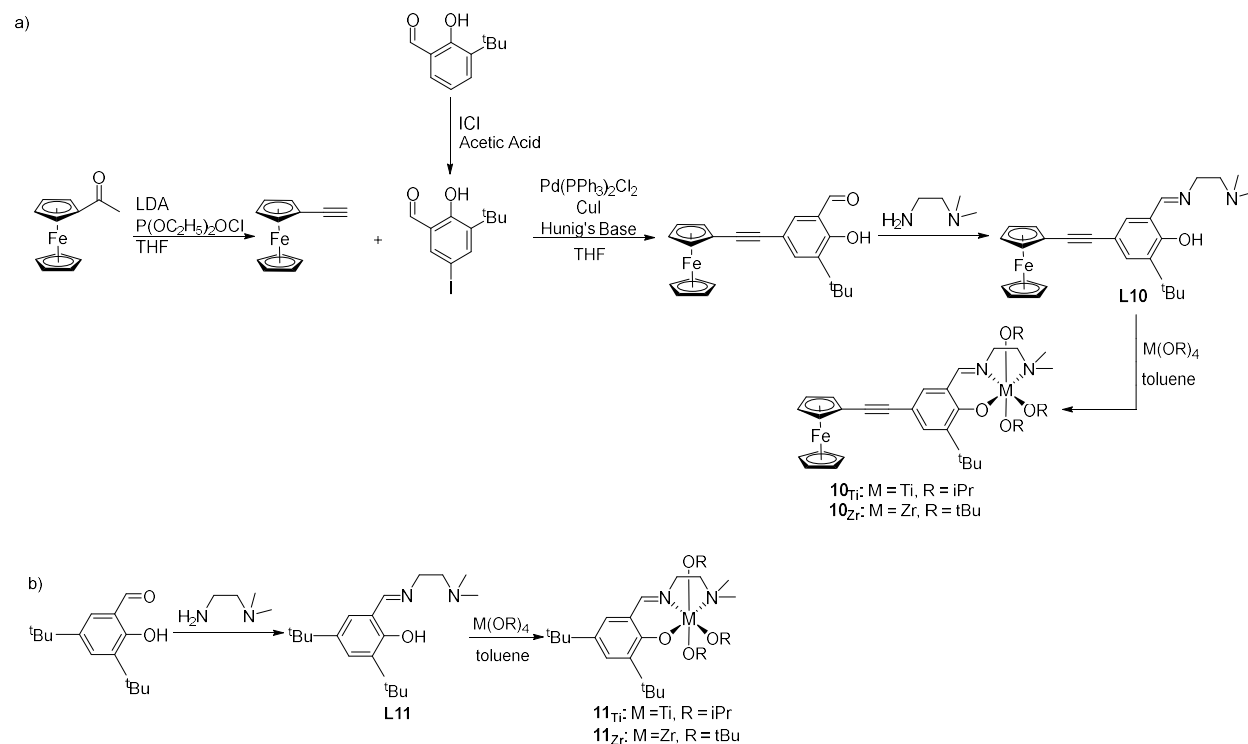
Tridentate [ONN] Schiff base-type ligands were chosen for this study due to their structural similarity to catalyst **1**,⁹⁰ straightforward synthesis, and because they have been previously studied as ROP catalysts in conjunction with various other metal centers such as In,^{152, 153} Zn,¹⁵⁴⁻¹⁵⁷ Ca,¹⁵⁷⁻¹⁵⁹ Sn,¹⁶⁰ and Ni.¹⁶¹ However, to the best of our knowledge, these tridentate [ONN] ligands have not been employed with group IV transition metal centers, nor their utility in RSC probed and compared to their symmetric tetradentate analogues. Therefore, we herein report the synthesis and RSC behavior of [ONN] Schiff base-type catalysts **10_{Ti}** and **10_{Zr}** for the ROP of LA. Their polymerization behavior is compared to symmetric tetradentate catalyst **1**, as well as their analogous tridentate Schiff base-type catalysts that do not contain redox-active ferrocenyl moieties (**11_{Ti}** and **11_{Zr}**).

2.2 Results and Discussion

Catalysts **10_{Ti}** and **10_{Zr}** were synthesized as shown in **Scheme 2.1a**, starting from commercially available acetylferrocene and 3-tert-butylsalicylaldehyde. Ethynylferrocene was obtained from acetylferrocene using LDA and diethyl chlorophosphite while 3-tert-butyl-5-iodosalicylaldehyde was obtained from 3-tert-butylsalicylaldehyde using iodomonochloride following previously reported literature procedures.^{162, 163} Ethynylferrocene and 3-tert-butyl-5-iodosalicylaldehyde were then coupled using Sonogashira coupling to obtain 3-tert-butyl-5-ethynylferrocene-salicylaldehyde.⁹⁰ Ligand **L10** was synthesized via condensation of N,N-

dimethylethylenediamine onto 3-tert-butyl-5-ethynylferrocene-salicylaldehyde and metallated using either $\text{Ti}(\text{O}^i\text{Pr})_4$ or $\text{Zr}(\text{O}^i\text{Bu})_4$ to yield catalysts **10_{Ti}** and **10_{Zr}**, respectively. Because analogous group IV transition metal-based ROP catalysts bearing tridentate [ONN] Schiff base ligands have not been previously reported, we also sought to compare the activity of catalysts **10_{Ti}** and **10_{Zr}** to their non-ferrocenyl substituted analogues **11_{Ti}** and **11_{Zr}**.

Scheme 2.1 Synthesis of [ONN]-type Catalysts (a) **10_{Ti}**, **10_{Zr}**, (b) **11_{Ti}**, and **11_{Zr}**



Ligand **L11** was synthesized via condensation of *N,N*-dimethylethylenediamine onto commercially available 3,5-di-tert-butyl-2-hydroxybenzaldehyde¹⁵⁴ and subsequently metallated using $\text{Ti}(\text{O}^i\text{Pr})_4$ to yield catalyst **11_{Ti}**, whereas metallation with $\text{Zr}(\text{O}^i\text{Bu})_4$ yielded catalyst **11_{Zr}** (**Scheme 2.1b**). Catalysts **10_{Ti}**, **10_{Zr}**, **11_{Ti}**, and **11_{Zr}** were each characterized using standard analytical techniques and their structures confirmed by single-crystal X-ray diffraction. Therein, crystallographic quality crystals of **10_{Ti}** and **10_{Zr}** were produced via recrystallization from hexanes, whereas crystals of **11_{Ti}** and **11_{Zr}** were produced via recrystallization from pentane at -20 °C. Catalysts **10_{Ti}**, **10_{Zr}**, **11_{Ti}**, and **11_{Zr}** were all found to adopt a distorted octahedral geometry as seen in **Figure 2.2**.

The L-LA ROP activity of catalysts **10_{Ti}**, **10_{Zr}**, **11_{Ti}**, and **11_{Zr}** were evaluated at 90 °C in C_6D_6 via ^1H NMR spectroscopy. A plot of monomer conversion (%) versus polymerization time (h) for each catalyst is shown in **Figure 2.3**. We found that catalyst **10_{Ti}** reached 90% monomer conversion in 20 h ($k_{\text{obs}} = 0.15 \pm 0.003 \text{ h}^{-1}$) (**Figure A.35**), whereas catalyst **10_{Zr}** proved to be significantly more active, reaching 90% monomer conversion in only 4.5 h ($k_{\text{obs}} = 0.8 \pm 0.1 \text{ h}^{-1}$) (**Figures A.39**). Similarly, when comparing catalyst **11_{Ti}** and **11_{Zr}**, the Zr-based catalyst **11_{Zr}** ($k_{\text{obs}} = 0.83 \pm 0.05 \text{ h}^{-1}$ (**Figure A.46**)) displayed a significantly higher activity than **11_{Ti}** ($k_{\text{obs}} = 0.25 \pm 0.05 \text{ h}^{-1}$ (**Figure A.45**)). These findings correlate well with previous studies that have shown that Zr-based catalysts tend to have higher activities for the ROP of LA than their Ti-based analogues.¹⁶⁴⁻¹⁶⁷ This is believed to be due to the larger ionic

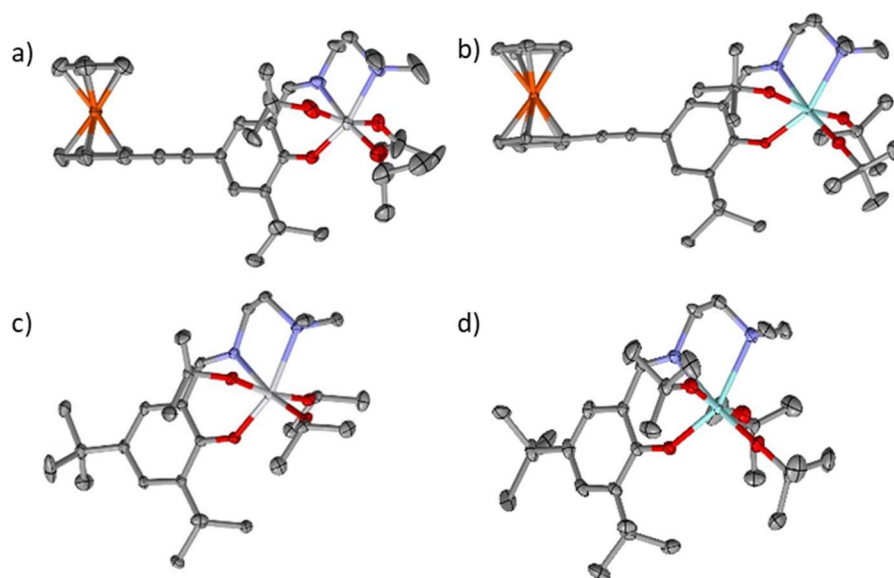


Figure 2.2 X-ray crystallographic structures of catalysts (a) **10_{Ti}**, (b) **10_{Zr}**, (c) **11_{Ti}**, and (d) **11_{Zr}** represented using ShelXle. Thermal ellipsoids are drawn at 50% probability and all hydrogens and solvent molecules are excluded for clarity.

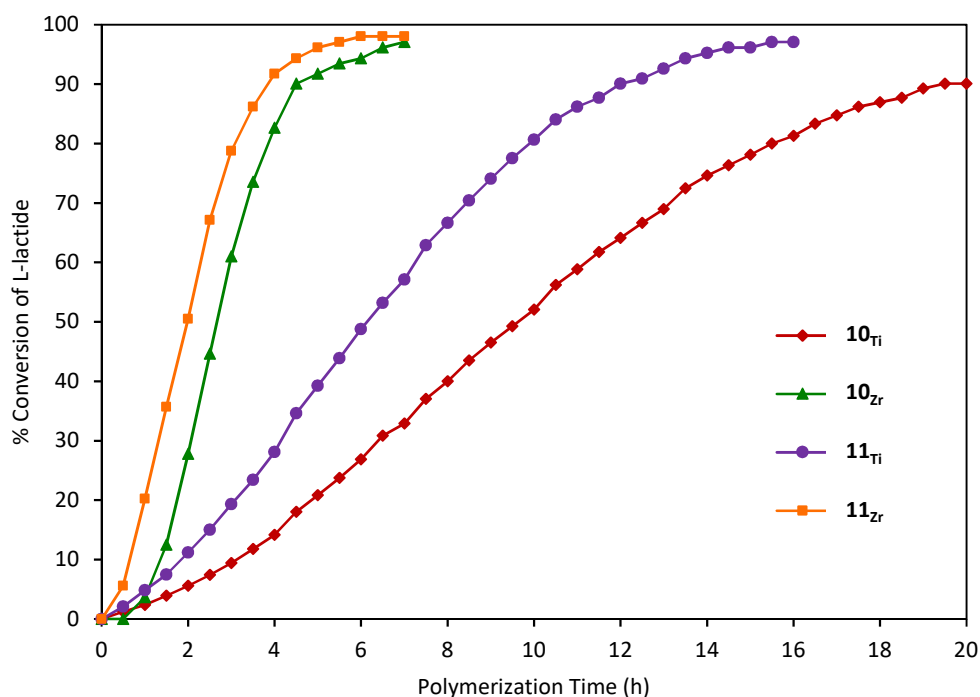


Figure 2.3 Plot of monomer conversion (%) versus time (h) for the polymerization of L-LA (100 eq, 1 M) as determined by ¹H NMR spectroscopy in C₆D₆ at 90 °C using catalysts **10_{Ti}** (red diamonds), **10_{Zr}** (green triangles), **11_{Ti}** (purple circles), and **11_{Zr}** (orange squares).

radius and coordination sphere of Zr, which results in a less sterically crowded site for monomer coordination.^{106, 165, 166} Additionally, DFT calculations by Diaconescu and coworkers have shown that for Ti- and Zr-based thiolan catalysts, Zr exhibits a higher effective nuclear charge than Ti (Mulliken charge = 1.44 vs. 1.14, respectively) which results in a stronger interaction between the carbonyl of the monomer and the metal center. This strengthening of monomer coordination lowers the overall energy barriers of polymerization and leads to a more active polymerization catalyst when using Zr as the active metal center, as compared to Ti.⁹⁶ We hypothesize that a similar combination of steric and electronic effects also contribute to the difference in activity observed between catalysts **10_{Ti}** and **10_{Zr}** and **11_{Ti}** and **11_{Zr}**.

To characterize the polymers produced by catalysts **10_{Ti}**, **10_{Zr}**, **11_{Ti}**, and **11_{Zr}**, larger scale polymerizations were conducted using each catalyst (**Table 2.1**). Due to the large disparity in rates of polymerization observed for each catalyst, all polymerizations were quenched at approximately 80% monomer conversion, in lieu of holding reaction time constant. Upon isolation of those polymers, we observed that each catalyst yields polymers with similar low dispersities ($\text{Đ} \leq 1.4$) and relatively similar molecular weights ($M_n = 6.8\text{--}8.3$ kg/mol) (**Table 2.1**). Experimental M_n values are lower than theoretical M_n values (**Table 2.1**) predicted based upon one polymer chain per metal center. It has been reported that related group IV-based ROP catalysts may produce two polymer chains per metal center (so-called dual propagation);^{91, 92} however, our experimental M_n values are higher than those expected for dual propagation. These results suggest that catalysts **10_{Ti}**, **10_{Zr}**, **11_{Ti}**, and **11_{Zr}** may produce either one or two chains per metal center, or more likely that they produce two chains per metal center, albeit only a portion of the added catalyst is polymerization active.

The redox-activity of ferrocenyl-substituted catalysts **10_{Ti}** and **10_{Zr}** were evaluated using cyclic voltammetry (CV) with dichloromethane as the solvent, $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.2 M) as the supporting electrolyte, and operating at a scan rate of 100 mV/s. The redox potentials ($E_{1/2}$) of **10_{Ti}** and **10_{Zr}** were -0.03 V and 0.03 V, respectively, versus a Fc/Fc^+ standard (**Figure 2.4**). These $E_{1/2}$ values are consistent with the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox couple of a ligand-based ferrocenyl moiety and are in good agreement with that measured for catalyst **1** ($E_{1/2} = 0.08$ V). Silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (AgBAR^{F}) and cobaltocene (CoCp_2) were chosen as suitable oxidizing and reducing agents, respectively, as their equivalent electrochemical potentials are sufficient to achieve the ferrocene/ferrocenium transition, as measured by CV.¹⁶⁸

Polymerizations of L-LA using catalyst **10_{Ti}** in its native, oxidized (**10_{Ti-ox}**, generated via the addition of 1 equiv. AgBAR^{F} to **10_{Ti}**), and reduced (**10_{Ti-red}**, generated via the addition of 1 equiv. CoCp_2 to **10_{Ti-ox}**) ligand states were conducted in C_6D_6 at 90 °C (sealed tube) and monitored via ^1H NMR spectroscopy. Therein, catalyst **10_{Ti}** reached 90% conversion in 20 h ($k_{\text{obs}} = 0.15 \pm 0.003$ h⁻¹) (**Figure A.35**), whereas oxidized catalyst **10_{Ti-ox}** reached only ~5% monomer conversion in the same period of time ($k_{\text{obs}} = 0.01 \pm 0.002$ h⁻¹) (**Figure 2.5a** and **A.36**). We hypothesize that this difference in activity between **10** and **10_{ox}** is due to the formation of a highly stabilized five membered metallocycle when using **10_{ox}**, which makes propagation thermodynamically unfavorable. Such behavior has previously been reported by Diaconescu for related redox-switchable catalysts.⁹⁴

This initial result suggests that oscillation between these two redox-states should yield an effective redox-switch in polymerization activity. However, we instead found that reduced catalyst **10_{Ti-red}**, which was expected to behave identically to native catalyst **10_{Ti}**, exhibited an initial polymerization rate greater than **10_{Ti}**, and that all polymerization activity ceased prior to 50% monomer conversion. The discrepancy in polymerization behavior between catalysts **10_{Ti}** and **10_{Ti-red}** suggests that one or more deleterious side reactions occur during the oxidation and/or reduction of the catalyst, thereby generating a new catalyst species (**10_{Ti-red}**) that is chemically distinct from

Table 2.1 Polymerization of L-LA using Catalysts **10_{Ti}**, **10_{Zr}**, **11_{Ti}**, and **11_{Zr}**.^a

Catalyst	Time (h)	Conv. ^b (%)	M _n ^c (g/mol)	M _n ^d (theo.)	<i>Đ</i> ^c
10_{Ti}	20.0	80	8,300	11,500	1.38
10_{Zr}	4.5	83	8,000	12,000	1.18
11_{Ti}	12.5	79	6,800	11,400	1.36
11_{Zr}	4.0	81	8,200	11,600	1.21

^aPolymerization Conditions: 1.0 mmol L-LA, 0.01 mmol catalyst, 1 mL benzene, 90 °C. All polymerizations were ran to approximately 80% monomer conversion. ^bDetermined based upon isolated polymer yield. ^cDetermined using triple detection gel permeation chromatography at 30 °C in THF. ^dTheoretical M_n values were calculated based upon conversion and assuming one polymer chain per metal center.

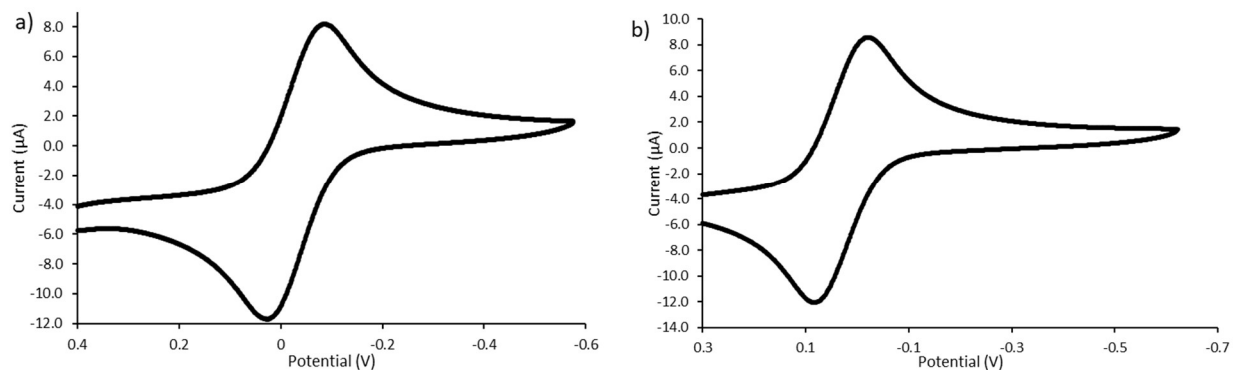


Figure 2.4 Cyclic voltammogram recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), with (nBu)₄NPF₆ (0.20 M) for (a) **10_{Ti}** (0.01 mmol) (*E*_{1/2} = -0.03 V) versus Fc/Fc⁺, and (b) **10_{Zr}** (0.01 mmol) (*E*_{1/2} = 0.03 V) versus Fc/Fc⁺.

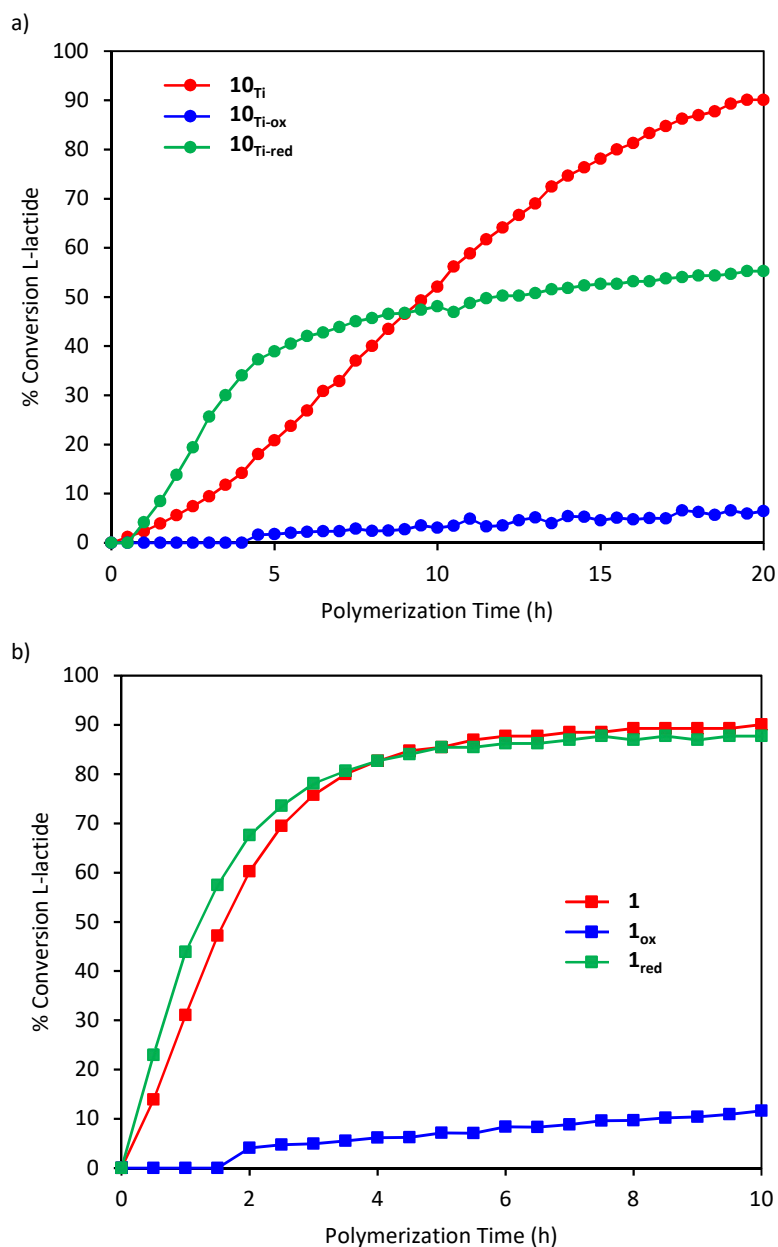


Figure 2.5 Plot of monomer conversion (%) versus time (h) for the polymerization of L-LA (100 eq, 1 M) as determined by ^1H NMR spectroscopy in C_6D_6 at 90°C using (a) 10_{Ti} (red circles), 10_{Ti-ox} (blue circles), and 10_{Ti-red} (green circles) and (b) 1 (red squares), 1_{ox} (blue squares), and 1_{red} (green squares).

catalyst **10_{Ti}**. This hypothesis is supported by ¹H NMR spectroscopy which shows that oxidation and reduction of **10_{Ti}** (to form **10_{Ti-red}**) yields one or more species that are chemically distinct from **10_{Ti}** (**Figure 2.6**). For example, the peak corresponding to the methyl protons of the -OⁱPr ligands of catalyst **10_{Ti}** integrates to 18H, but when AgBAR^F is added to generate **10_{Ti-ox}**, the integration of this peak decreases to 12H and a new peak at 1.3 ppm with an integration of 6H appears. We speculate that this may be due to the formation of AgOⁱPr,^{169, 170} however, further experimentation or computational studies are needed to support this hypothesis. In an attempt to circumvent these deleterious side reactions, analogous polymerizations were conducted using other solvents (CDCl₃) (**Figure A.16**) and oxidants such as AgOTf, ^{Ac}FcBAR^F, and trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, though no improvement was observed.

To compare the relative rates of polymerization for asymmetric tridentate catalyst **10_{Ti}** to those of symmetric tetradentate catalyst **1** (**Figure 2.5b**), analogous polymerizations were performed using catalysts **1**, **1_{ox}**, and **1_{red}**. During these studies, we discovered that oxidation of **1** with AgBAR^F (2 equiv.) yielded inconsistent results. Instead, AgOTf (2 equiv.) was used as the oxidizing agent for catalyst **1**, as was previously used by Gibson and Long.⁹⁰ Comparison of these catalysts revealed that **10_{Ti}** polymerizes L-LA approximately 3× slower than **1**, ultimately reaching 90% monomer conversion in 20 h ($k_{\text{obs}} = 0.15 \pm 0.003 \text{ h}^{-1}$) whereas catalyst **1** reaches the same conversion in approximately 6 h ($k_{\text{obs}} = 0.49 \pm 0.06 \text{ h}^{-1}$) (**Figure A.32**). Oxidized catalysts **10_{Ti-ox}** and **1_{ox}** both exhibit a drastic decrease in polymerization rate relative to their native catalyst species, achieving ≤ 10% monomer conversion in 20 and 10 h, respectively (**Figure A.33**). However, it should be noted that the polymerization rate of **1_{ox}** is notably faster than that of **10_{Ti-ox}**.

Differentiation in polymerization activity between native and oxidized states of catalysts **10_{Ti}** and **1** were similar, yielding $k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$ ratios of 57 (± 14) and 44 (± 23) for catalysts **1** and **10_{Ti}**, respectively (**Figures 2.7** and **A.47**). However, in contrast to catalyst **10_{Ti}**, which is unstable under oxidation and/or reduction conditions, reduced catalyst **1_{red}** polymerizes L-LA with a virtually identical rate as native catalyst **1** ($k_{\text{obs}} = 0.52 \pm 0.05 \text{ h}^{-1}$ versus $k_{\text{obs}} = 0.49 \pm 0.06 \text{ h}^{-1}$) (**Figure A.34**) clearly indicating that catalyst **1** exhibits greater stability to oxidation and reduction than **10_{Ti}**. These results also support that catalysts bearing tridentate [ONN] ligands with a single ferrocenyl moiety may exhibit similar differentiation in catalytic activity (between native and oxidized states) to symmetric catalysts bearing a tetradentate [ONNO] ligand and two ferrocenyl moieties, albeit at lower overall rates. However, the mechanistic rationale for the observed difference in activity between **1** and **10_{Ti}** ($k_{\text{obs}} = 0.49 \pm 0.06$ and $0.15 \pm 0.003 \text{ h}^{-1}$, respectively), yet similar redox-switchability (57 (± 14) and 44 (± 23), respectively) despite changes in ligand denticity and number of redox-active moieties, is not well understood at this time.

To further investigate this class of catalysts, and to probe the effect metal center identity plays on catalytic activity and redox-switchability, we examined the analogous Zr-based catalyst, **10_{Zr}**. Monitoring the oxidation and reduction of catalyst **10_{Zr}** via ¹H NMR spectroscopy revealed controlled oxidation and reduction behavior with catalyst **10_{Zr-red}** being spectroscopically identical to the native **10_{Zr}** species (**Figure 2.8**). Though we hypothesize that the oxidation and reduction reactions occur at the ferrocenyl-based Fe-center ($E_{1/2} = 0.03 \text{ V}$ versus a Fc/Fc⁺ standard), it should be noted that the ¹H NMR resonances of **10_{Zr-ox}** did not broaden as significantly as might be expected following the formation of a paramagnetic ferrocenium-based complex. Attempts to confirm oxidation of the ferrocenyl moiety via UV-vis spectroscopy were inconclusive (**Figure A.21**); however, magnetic susceptibility measurements using Evan's NMR method suggest that native complex **10_{Zr}** is diamagnetic, whereas **10_{Zr-ox}** is paramagnetic ($\mu_{\text{eff}} = 1.17 \mu_{\text{B}}$), indicating that oxidation has occurred.

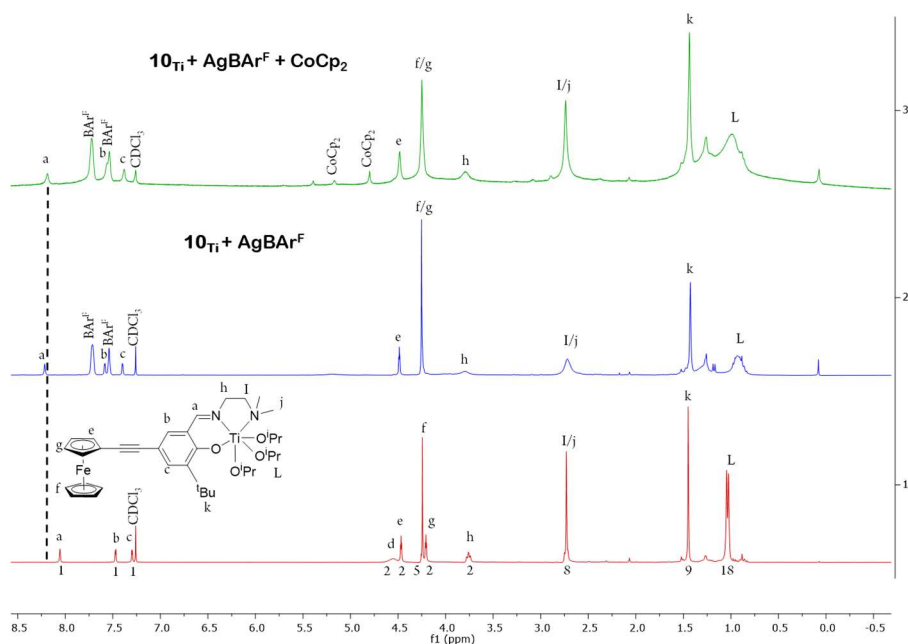


Figure 2.6 ^1H NMR spectra (300 MHz, 25 $^\circ\text{C}$, CDCl_3) of 10_{Ti} (bottom), $10_{\text{Ti-ox}}$ (middle), and $10_{\text{Ti-red}}$ (top). $10_{\text{Ti-ox}}$ was generated by the addition of AgBAR^{F} to 10_{Ti} in CDCl_3 followed by filtration into a J. Young NMR tube. $10_{\text{Ti-red}}$ was generated by the subsequent addition of CoCp_2 to the NMR tube. A shift in the peaks is seen between the bottom and middle spectra. Another shift in the peaks is seen between the middle and top spectra but the peaks in the top spectrum do not shift back to the same position as the peaks in the bottom spectrum.

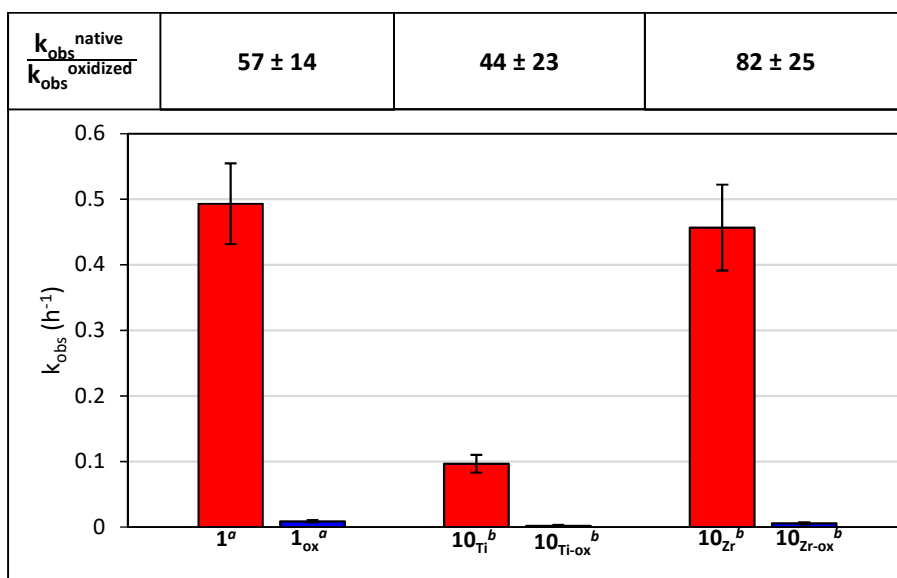


Figure 2.7 Comparison of k_{obs} for catalysts $1/1_{\text{ox}}$, $10_{\text{Ti}}/10_{\text{Ti-ox}}$, and $10_{\text{Zr}}/10_{\text{Zr-ox}}$. Conditions: 10 μmol catalyst, 0.7 mmol L-LA, 1 M, 90 $^\circ\text{C}$. $^{\text{a}}$ solvent = C_6D_6 , $^{\text{b}}$ solvent = CDCl_3 .

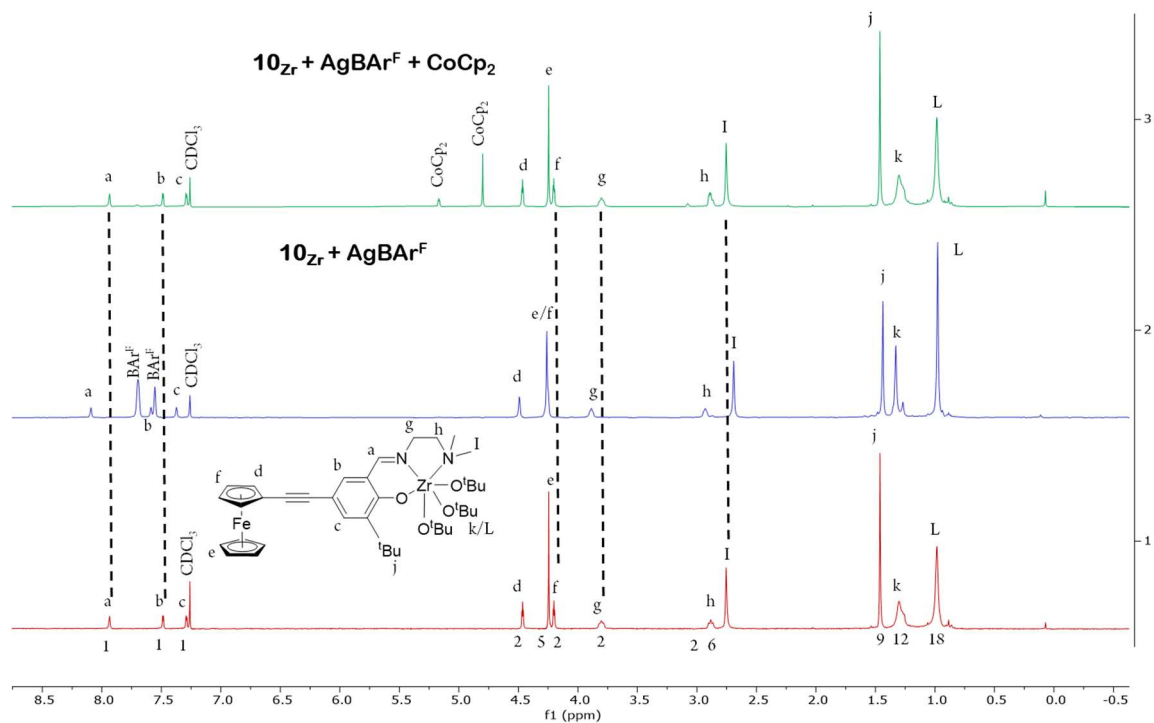


Figure 2.8 ^1H NMR spectra (300 MHz, 25 $^\circ\text{C}$, CDCl_3) of 10_{Zr} (bottom), $10_{\text{Zr-ox}}$ (middle), and $10_{\text{Zr-red}}$ (top). $10_{\text{Zr-ox}}$ was generated by the addition of AgBAR^{F} to 10_{Zr} in CDCl_3 followed by heating at 90 $^\circ\text{C}$ for 1 h in a J. Young NMR tube. $10_{\text{Zr-red}}$ was generated by the addition of AgBAR^{F} to 10_{Zr} in CDCl_3 followed by filtration into a new vial with CoCp_2 then addition to an NMR tube. A shift in the peaks is seen between the bottom and middle spectra. Another shift in the peaks is seen between the middle and top spectra with the peaks in the top spectrum shifting back to the same position as the peaks in the bottom spectrum.

The L-LA ROP behavior of **10_{Zr}**, **10_{Zr-ox}**, and **10_{Zr-red}** was likewise monitored at 90 °C via ¹H NMR spectroscopy. Plots of monomer conversion (%) versus polymerization time (h) are shown in **Figure 2.9**. In its native state, **10_{Zr}** reached 90% monomer conversion in 6 h ($k_{\text{obs}} = 0.46 \pm 0.07 \text{ h}^{-1}$) (**Figure A.40**), whereas **10_{Zr-ox}** (generated via the addition of 1 equiv. AgBAR^F to **10_{Zr}**) only reached approximately 5% monomer conversion in the same time period ($k_{\text{obs}} = 0.01 \pm 0.002 \text{ h}^{-1}$) (**Figure A.41**). Furthermore, the reduced catalyst, **10_{Zr-red}** (generated via the addition of 1 equiv. CoCp₂ to **10_{Zr-ox}**), polymerized L-LA with a rate similar to that of **10_{Zr}**, reaching 86% monomer conversion in 6 h ($k_{\text{obs}} = 0.34 \pm 0.09 \text{ h}^{-1}$) (**Figure 2.9** and **A.42**) and producing polymer of similar molecular weight and dispersity ($M_n = 6,200 \text{ g/mol}$, $\bar{D} = 1.03$) as catalyst **10_{Zr}** ($M_n = 7,000 \text{ g/mol}$, $\bar{D} = 1.06$). When comparing **10_{Zr}** to **10_{Ti}**, catalyst **10_{Zr}** was found to polymerize L-LA approximately 5× faster than **10_{Ti}**. However, unlike catalyst **10_{Ti}**, which is unstable under oxidation and/or reduction conditions, catalyst **10_{Zr-red}** polymerized L-LA with a rate similar to **10_{Zr}** indicating that **10_{Zr}** is stable to both oxidation and reduction. The greater stability of **10_{Zr}** is not well understood at this time and would require extensive investigation into the degradation of **10_{Ti}**, however, such studies are outside of the purview of our investigation.

Differentiation in the polymerization activity between the native and oxidized states of catalysts **10_{Ti}** and **10_{Zr}** was also drastically different, yielding $k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$ ratios of 44 (± 23) and 82 (± 25) for catalysts **10_{Ti}** and **10_{Zr}**, respectively (**Figure 2.7** and **A.47**). The larger difference in the $k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$ ratios of catalyst **10_{Zr}**, as compared to **10_{Ti}**, suggests that upon oxidation, the five membered metallocycle intermediate formed following monomer ring-opening is more greatly stabilized for **10_{Zr-ox}**, as compared to **10_{Ti-ox}**, resulting in a lower polymerization rate. This is believed to arise due to the greater electrophilicity of the Zr-center as compared to Ti.

Lastly, it should be noted that addition of excess CoCp₂ during the generation of **10_{Zr-red}** results in an increased rate of polymerization as compared to **10_{Zr}** (**Figure A.17**). We hypothesize that this may be due to the Lewis acidity of CoCp₂ that may interact with the monomer. This is supported by analogous polymerizations in which CoCp₂ (1 equiv.) was added to native catalyst **10_{Zr}**, resulting in an increased polymerization rate as compared to polymerization using only **10_{Zr}**. ¹H NMR spectroscopy further suggests that CoCp₂ does not alter or interact with **10_{Zr}**, though further experimental or computational investigations are required to elucidate the mechanistic nature of this observation.

The *in situ* redox-switchability of **10_{Zr}** was evaluated via sequential addition of redox reagents and monitored via ¹H NMR spectroscopy (**Figure 2.10**). Therein, the polymerization activity of catalyst **10_{Zr}** was first monitored at 90 °C in CDCl₃ for 2.5 hours, during which time monomer conversion reached 30%. AgBAR^F was then added to the polymerization mixture, generating **10_{Zr-ox}** *in situ*. Following addition of oxidant, all polymerization activity ceased and no measurable increase in monomer conversion was detected for 2 hours. Finally, CoCp₂ was added to the polymerization mixture to generate **10_{Zr-red}**, and as expected, polymerization activity was restored at a rate similar to that of **10_{Zr}** prior to oxidation. These results support that **10_{Zr}** can indeed be used for RSC through redox modulation of **10_{Zr}**'s single ferrocenyl moiety, and this switching behavior is retained after multiple consecutive *in situ* switches (**Figure A.44**).

2.3 Conclusion

Our results demonstrate that asymmetric catalyst **10_{Ti}**, which bears a tridentate [ONN] ligand and only one ferrocenyl moiety, and symmetric catalyst **1**, which bears a tetradentate [ONNO] ligand featuring two ferrocenyl moieties, are both active for the ROP of L-LA in their native states and dramatically less active in their

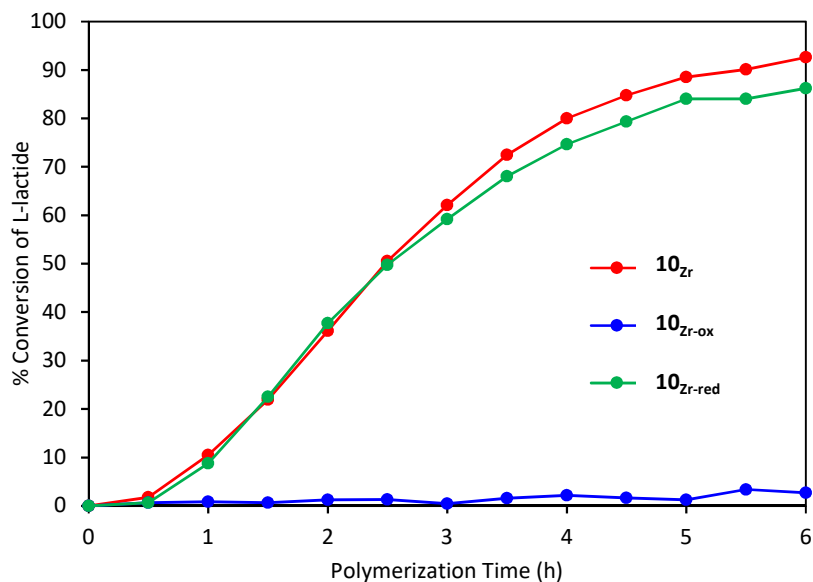


Figure 2.9 Plot of monomer conversion (%) versus time (h) for the polymerization of L-LA (100 eq, 1 M) as determined by ^1H NMR spectroscopy in CDCl_3 at 90°C using 10_{Zr} (red circles), $10_{\text{Zr-ox}}$ (blue circles), and $10_{\text{Zr-red}}$ (green circles).

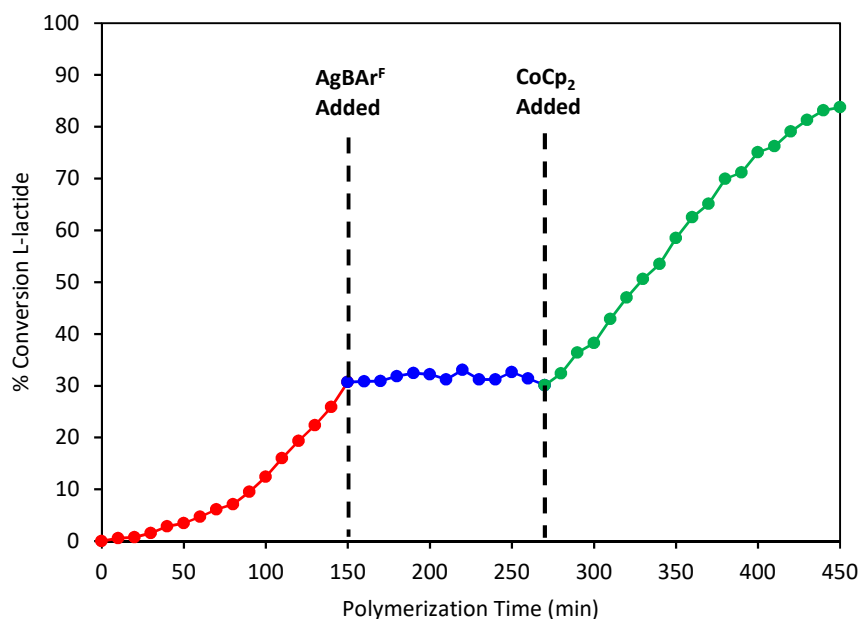


Figure 2.10 Plot of monomer conversion (%) versus time (min) for the *in situ* redox-switching polymerization of L-LA (100 eq, 1 M) as determined by ^1H NMR spectroscopy in CDCl_3 at 90°C . Catalyst 10_{Zr} (red circles), oxidation with AgBAR^{F} to produce $10_{\text{Zr-ox}}$ (blue circles), and reduction to $10_{\text{Zr-red}}$ (green circles) using CoCp_2 .

oxidized states, albeit catalyst **10_{Ti}** polymerizing L-LA approximately 3× slower than **1**. Differentiation in catalytic polymerization activity, as defined by the “on/off” ratio of $k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$, was found to be within error of one another displaying effective on/off ratios for catalysts **1** and **10_{Ti}** of 57 (± 14) and 44 (± 23), respectively. These results suggest that the number of ferrocenyl moieties may not play a crucial role in these catalysts’ ability to differentiate catalytic activity as a function of ligand-based oxidation state, but ligand denticity may indeed impact polymerization rates.

Though catalyst **1** proved to be stable to both oxidation and reduction, we found that asymmetric catalyst **10_{Ti}** undergoes deleterious side reactions during oxidation and/or reduction, regardless of polymerization solvent and oxidant used, generating a new catalyst species (**10_{Ti-red}**) that is chemically distinct from **10_{Ti}**. This suggests that tridentate [ONN] ligands may be insufficient to stabilize the catalytically active Ti-based species during sequential oxidations and reductions.

In contrast to catalyst **10_{Ti}**, catalyst **10_{Zr}** proved to be stable to both oxidation and reduction, as evidenced by ¹H NMR spectroscopy. Catalyst **10_{Zr}** exhibited a rate of polymerization approximately 5× faster than that of **10_{Ti}** and exhibited well-controlled redox switching behavior in which catalyst **10_{Zr-red}** polymerized L-LA with a remarkably similar rate to the native **10_{Zr}**. Lastly, differentiation in the polymerization activity of catalyst **10_{Zr}** based upon ligand-based oxidation state was roughly double ($k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}} = 82 (\pm 25)$) that of its analogous Ti-based catalyst **10_{Ti}**. This suggests that the identity of the active metal center may drastically influence catalytic stability, activity, and overall redox-switchability.

While the studies discussed herein have allowed us to experimentally observe how systematic changes in ligand architecture, namely ligand denticity and the number of redox-active moieties, affect catalytic behavior for the redox-switchable ROP of LA, they do not fully reveal the mechanistic rationale behind these observations. Computational examination of the mechanistic details for each catalyst in the native and oxidized states would provide valuable insight and a deeper understanding of how changes in ligand structure affect catalytic activity. These investigations may be the subject of future investigations in the Long group.

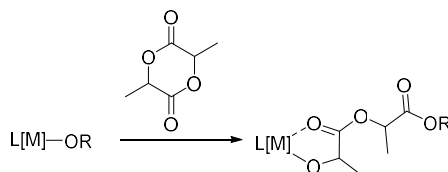
Chapter 3 – Redox-Switchable Ring-Opening Polymerization Behavior of [ONNO]-Type Salen and Salan Titanium and Zirconium Catalysts

3.1 Introduction

To further our investigation into the structure-catalytic performance relationship of redox-active ROP catalysts we examined how changes in ligand connectivity and conjugation affect catalytic activity, selectivity, and redox-switchability. All of the previously discussed catalysts (**1**, **10_{Ti}**, **10_{Zr}**), bear salen-type ligands which feature imine functionalities. In these complexes, the ligand scaffold is fully conjugated from the ferrocenyl moieties to the active metal center through both the phenolic and imine moieties, offering two potential paths by which electron-density may be donated or withdrawn upon oxidation or reduction of the ferrocenyl moieties. In order to probe how important electronic communication through the imine N's is to catalytic performance, we sought to isolate these functionalities so that electron transfer may occur only through the phenolic portion of the ligand. To accomplish this, a salan-type ligand which features amine functionalities is utilized.

Upon catalyst oxidation, the electron-density at the active metal center is decreased relative to the native catalyst increasing the electrophilicity of the metal center. It has previously been shown that this increase in electrophilicity of the metal center strengthens the coordination of the carbonyl to the active metal center leading to stabilization of the five membered metallocycle intermediate (**Scheme 3.1**) making dissociation of the carbonyl and subsequent coordination-insertion of another monomer (propagation) thermodynamically unfavorable.⁹⁴ However, we hypothesize that if electronic communication is lessened when conjugation through the imine moieties of the ligand is eliminated (salan-type catalyst), then the electrophilicity, and therefore stability of the five membered metallocycle intermediate, may not increase as much for the oxidized catalyst relative to the native catalyst. This could, therefore, result in a greater differentiation in polymerization behavior for the salen-type (imine containing) catalyst than the salan-type (amine containing) catalyst.

Scheme 3.1 Formation of the five membered metallocycle intermediate after the initial insertion of LA



Salan-type ligands were chosen for this study as non-redox-active salan catalysts with group IV metal centers have previously been shown to be active for the polymerization of cyclic esters.¹⁶⁶ However, to the best of our knowledge, salan-type catalysts with redox-active moieties distal to the active metal center have yet to be examined or compared to the analogous salen-type catalysts. Therefore, we sought to compare the catalytic activity, selectivity, and redox-switchability of group IV-based catalysts bearing salen-type ligands with two redox-active moieties (**1**) to those bearing salan-type ligands with two redox-active moieties (**12**) (**Figure 3.1**). Additionally, we will continue to examine the effect of metal center identity on catalytic performance by studying both the Ti- and Zr-centered analogues of each ligand. We herein report, the synthesis and RSC behavior of four [ONNO] salen- or salan-type catalysts (**1_{Ti}**, **1_{Zr}**, **12_{Ti}**, and **12_{Zr}**) for the ROP of L-LA and CL.

3.2 Results and Discussion

Catalysts **1_{Ti}**, **1_{Zr}**, **12_{Ti}**, and **12_{Zr}** were synthesized as shown in **Scheme 3.2**. Ligand **L1** was obtained via the condensation of 3-tert-butyl-5-ethynylferrocene-salicylaldehyde onto ethylenediamine following a literature

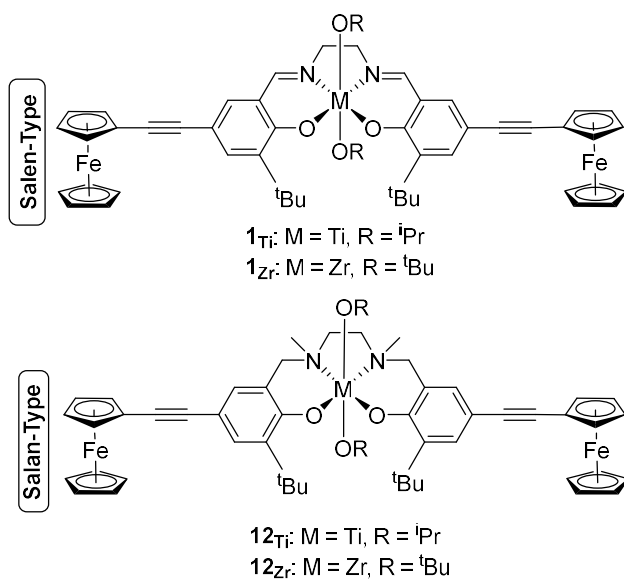
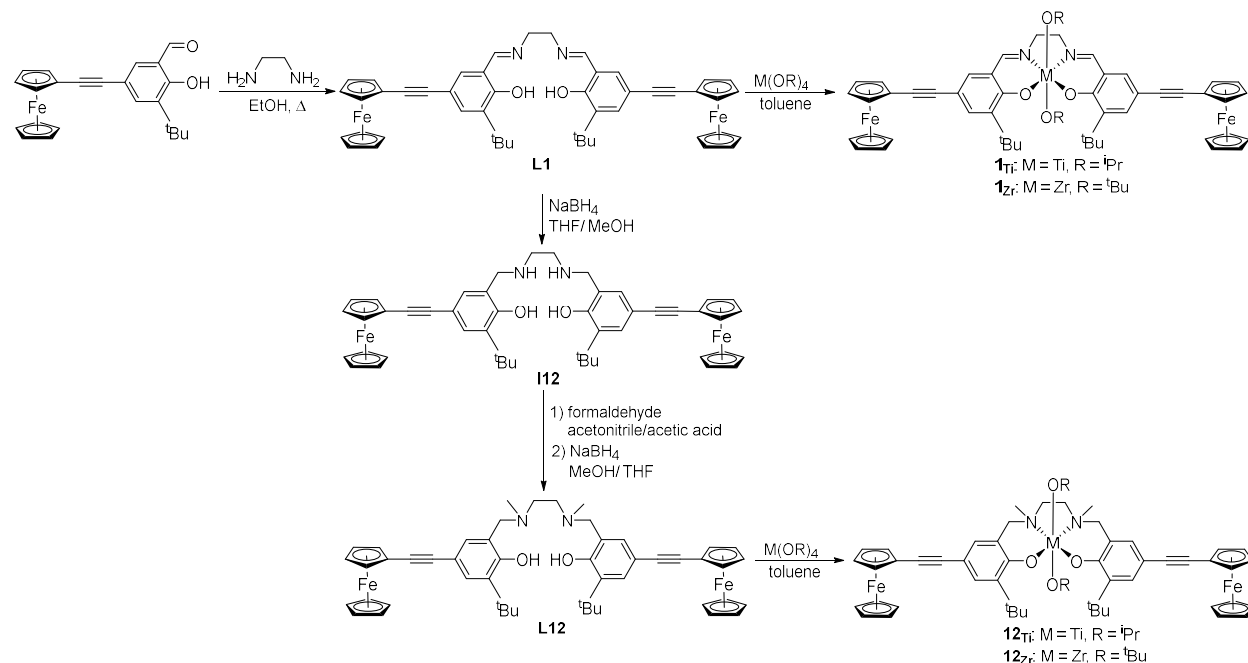


Figure 3.1 Salen-type catalysts 1_{Ti} and 1_{Zr} as compared to salan-type catalysts 12_{Ti} and 12_{Zr} .

subsequently methylated with formaldehyde in an acetonitrile:acetic acid mixture followed by treatment with NaBH₄ in a THF:MeOH mixture to yield **L12**. Once obtained, **L1** and **L12** were metallated with either Ti(OⁱPr)₄ or Zr(OⁱBu)₄ in toluene to yield **1_{Ti}**, **1_{Zr}**, **12_{Ti}**, or **12_{Zr}**. All new compounds were characterized using standard analytical techniques.

Scheme 3.2 Synthesis of Salen- and Salan-Type Catalysts **1_{Ti}**, **1_{Zr}**, **12_{Ti}**, and **12_{Zr}**



The redox-activity of catalysts **1_{Zr}**, **12_{Ti}**, and **12_{Zr}** were evaluated using CV with dichloromethane as the solvent, [nBu₄N][PF₆] (0.2M) as the supporting electrolyte, and operating at a scan rate of 100 mVs⁻¹. The E_{1/2} of **1_{Zr}**, **12_{Ti}**, and **12_{Zr}** were found to be 0.03 V, -0.06 V, and 0.01 V, respectively, versus a Fc/Fc⁺ standard (**Figure 3.2**). These E_{1/2} values are consistent with the Fe^{II}/Fe^{III} redox couple of a ligand-based ferrocenyl moiety and are within good agreement with the value measured for **1_{Ti}** (E_{1/2} = 0.08 V). Based on these values, AgOTf and CoCp₂ were chosen as suitable oxidizing and reducing agents as 1) their equivalent electrochemical potentials are sufficient to achieve the ferrocene/ferrocenium transition as measured by CV,¹⁶⁸ and 2) AgOTf and CoCp₂ were used by Gibson, N. Long, and colleagues during the original investigation of catalyst **1_{Ti}**.⁹⁰

Polymerization of L-LA using **1_{Ti}**, **1_{Zr}**, **12_{Ti}**, and **12_{Zr}** in their native, oxidized (ex: **1_{Ti-ox}**, generated via the addition of 2 equiv. AgOTf to **1_{Ti}**), and reduced (ex: **1_{Ti-red}**, generated via the addition of 2 equiv. CoCp₂ to **1_{Ti-ox}**) ligand states were conducted in C₆D₆ at 90 °C (sealed tube) and monitored via ¹H NMR spectroscopy. Therein all four catalysts were seen to be more active in the native Fe(II) state than in the oxidized Fe(III) state but with varying overall rates (**Figure 3.3**). Catalyst **1_{Ti}** (**Figure 3.3a**) was found to reach 90% conversion in approximately 11 h (k_{obs} = 0.26 ± 0.01 h⁻¹) (**Figure A.63**), whereas the oxidized catalyst **1_{Ti-ox}** reached < 5% monomer conversion in the same period (k_{obs} = 0.002 ± 0.001 h⁻¹) (**Figure A.64**). The reduced form **1_{Ti-red}** polymerized L-LA with a rate similar to **1_{Ti}** reaching 90% conversion in 11 h (k_{obs} = 0.22 ± 0.01 h⁻¹) (**Figure A.65**). Similarly, catalyst **12_{Ti}** (**Figure 3.3c**) was found to reach 90% conversion in approximately 8 h (k_{obs} = 0.31 ± 0.02 h⁻¹) (**Figure A.69**), the oxidized catalyst

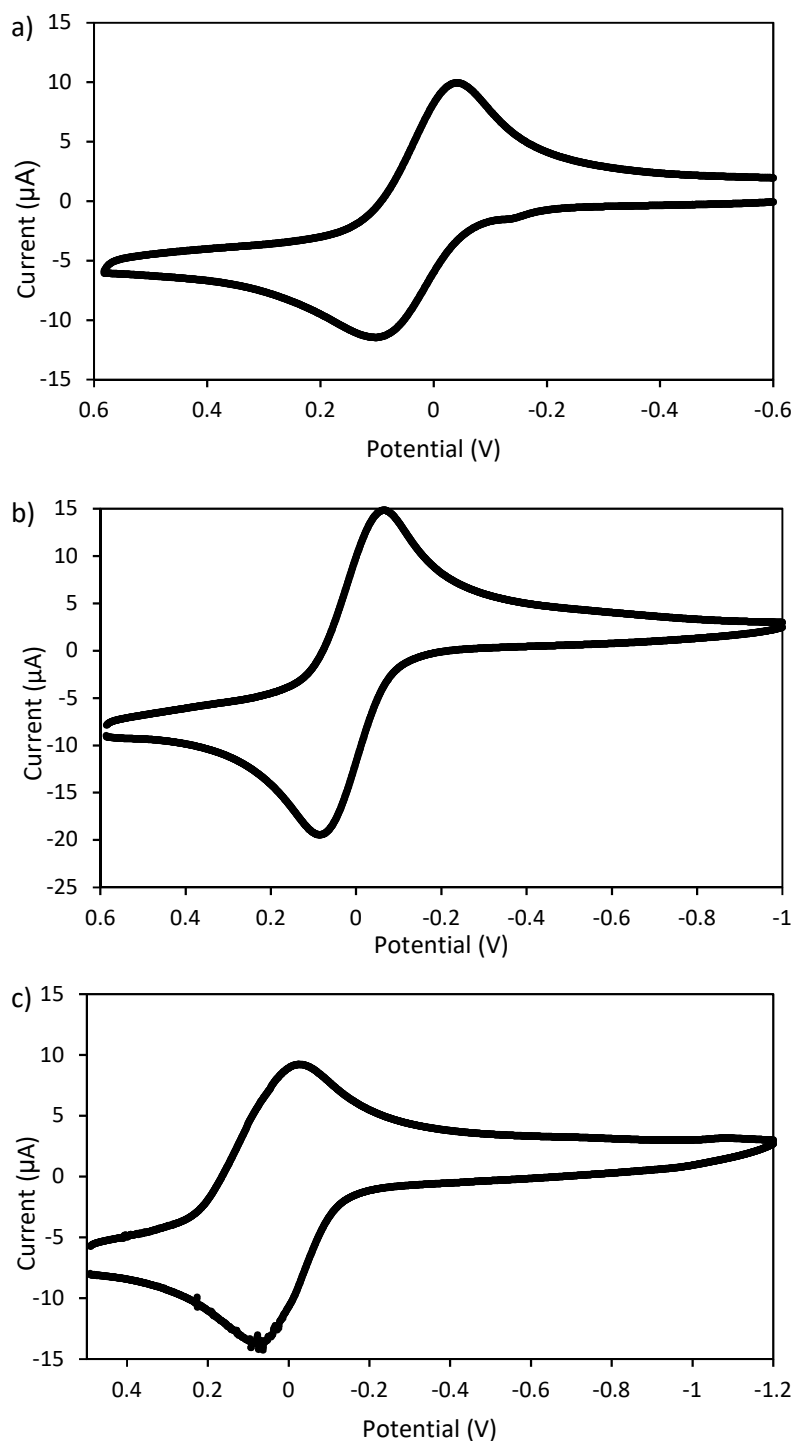


Figure 3.2 Cyclic voltammogram recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), with (nBu)₄NPF₆ (0.20 M) for (a) **1_{Zr}** ($E_{1/2} = -0.030$ V) versus Fc/Fc⁺, (b) **12_{Ti}** ($E_{1/2} = 0.012$ V) versus Fc/Fc⁺ and (c) **12_{Zr}** ($E_{1/2} = 0.020$ V) versus Fc/Fc⁺.

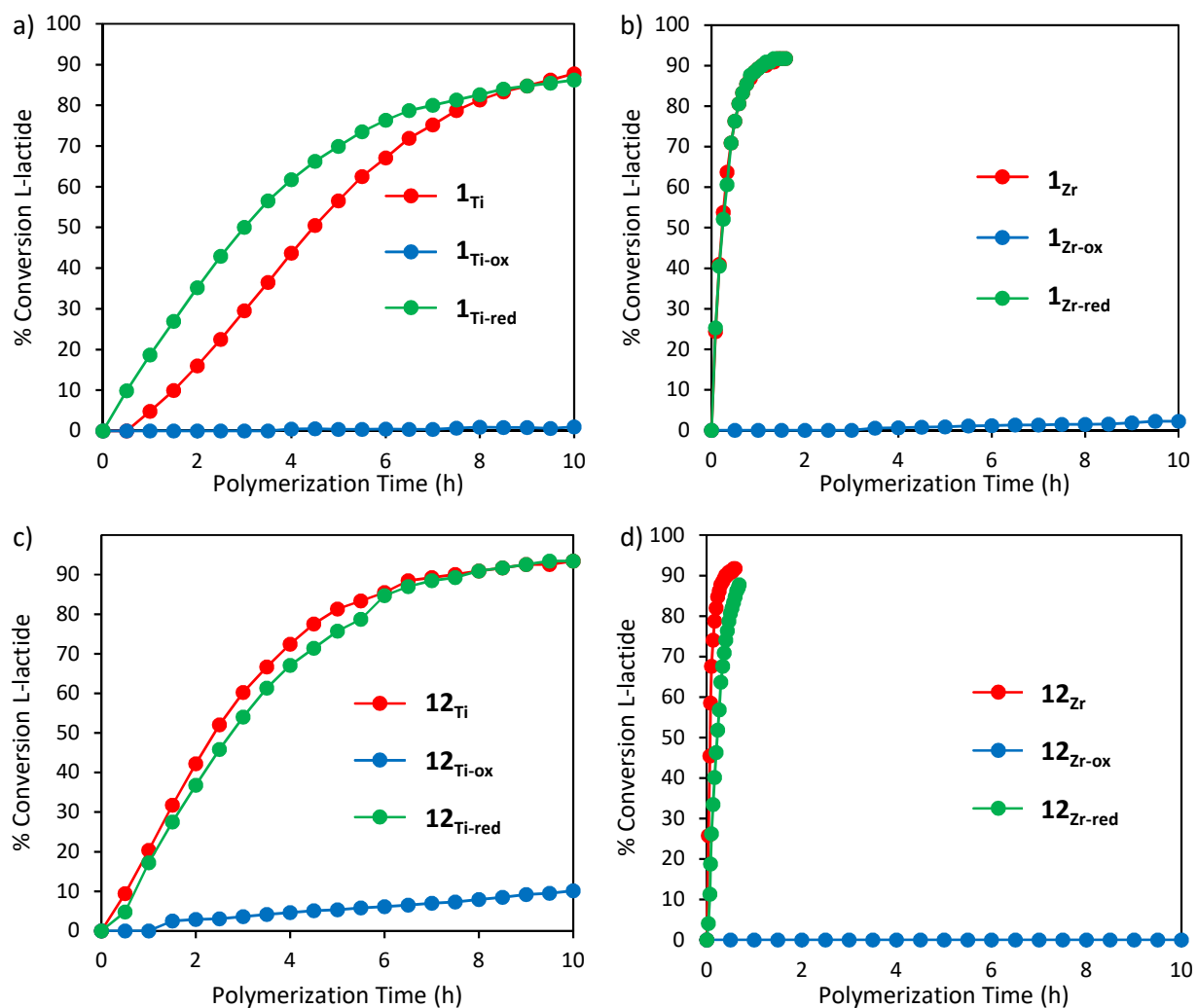


Figure 3.3 Plot of monomer conversion (%) versus time (h) for the polymerization of L-LA (100 eq, 1M) as determined by ^1H NMR spectroscopy in C_6D_6 at 90 $^\circ\text{C}$ using (a) 1_{Ti} (red circles), $1_{\text{Ti-ox}}$ (blue circles), and $1_{\text{Ti-red}}$ (green circles), (b) 1_{Zr} (red circles), $1_{\text{Zr-ox}}$ (blue circles), and $1_{\text{Zr-red}}$ (green circles), (c) 12_{Ti} (red circles), $12_{\text{Ti-ox}}$ (blue circles), and $12_{\text{Ti-red}}$ (green circles), and (d) 12_{Zr} (red circles), $12_{\text{Zr-ox}}$ (blue circles), and $12_{\text{Zr-red}}$ (green circles). Using AgOTf as an oxidizing agent and CoCp₂ as a reducing agent.

12-Ti-ox reached <10% monomer conversion in the same period ($k_{\text{obs}} = 0.01 \pm 0.0004 \text{ h}^{-1}$) (**Figure A.70**), and the reduced form **12-Ti-red** reached 90% conversion in 8 h ($k_{\text{obs}} = 0.26 \pm 0.04 \text{ h}^{-1}$) (**Figure A.71**).

Conversely, catalysts **1-Zr** and **12-Zr** (**Figure 3.3b** and **d**) were found to be significantly more active reaching 90% monomer conversion in approximately 1 h ($k_{\text{obs}} = 2.58 \pm 0.03 \text{ h}^{-1}$) (**Figure A.66**) and 0.3 h ($k_{\text{obs}} = 8.6 \pm 0.9 \text{ h}^{-1}$) (**Figure A.72**), respectively. In the oxidized state catalysts **1-Zr-ox** and **12-Zr-ox** exhibited significantly decreased activities reaching < 5% monomer conversion ($k_{\text{obs}} = 0.002 \pm 0.001 \text{ h}^{-1}$) (**Figure A.67**) and no observable polymerization ($k_{\text{obs}} = 0.00 \pm 0.00 \text{ h}^{-1}$) (**Figure A.73**), respectively, over 10 h. Catalyst **1-Zr-red** polymerized L-LA with a rate similar to **1-Zr** reaching 90% conversion in 1 h ($k_{\text{obs}} = 2.47 \pm 0.08 \text{ h}^{-1}$) (**Figure A.68**). Conversely, even though catalyst **12-Zr-red** was active for the polymerization of L-LA ($k_{\text{obs}} = 2.9 \pm 0.6 \text{ h}^{-1}$, **Figure A.74**), it exhibited a slower rate than **12-Zr** which reached 90% conversion in 0.3 h ($k_{\text{obs}} = 8.6 \pm 0.9 \text{ h}^{-1}$). This slightly decreased polymerization rate is believed to arise due to either 1) incomplete reduction of **12-Zr-red** upon addition of CoCp₂, or 2) partial catalyst decomposition upon oxidation and reduction, as indicated by the appearance of new peaks in both the aliphatic and aromatic regions of the NMR spectra of **12-Zr-red** (**Figure A.59**).

Comparison of the k_{obs} values of each catalyst in the native state was used to examine how ligand connectivity and metal center identity affect catalytic activity, while differentiation in polymerization activity between the native and oxidized catalyst state ($k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$) was used to examine how electronic communication of the ligand scaffold affects overall redox-switchability (**Figure 3.4**). As was seen in our previous study,⁹⁸ the Zr-based catalysts (**1-Zr** and **12-Zr**) exhibited higher activities and larger $k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$ ratios for the ROP of L-LA than their Ti-based analogues (**1-Ti** and **12-Ti**), indicating that metal center identity may play a significant role in both catalyst activity and redox-switchability. As previously discussed, it has been shown that analogous Zr-based catalysts exhibit a higher effective nuclear charge than Ti, which results in a strengthening of the interaction between the carbonyl of the monomer and the metal center.⁹⁶ This stronger coordination lowers the energy barriers of polymerization for the native complex leading to a more active catalyst. It is also hypothesized to more greatly stabilize the five membered metallocycle intermediate for the oxidized Zr complex, as compared to the Ti-based analogues, leading to a larger redox-switchability.⁹⁶

To examine how changes in ligand structure affect catalytic activity for the polymerization of L-LA, the native state activity of catalysts bearing the same metal center were compared (**1-Ti** vs. **12-Ti** and **1-Zr** vs. **12-Zr**). When compared, both salan-type catalysts (amine containing) were found to be more active than their salen-type (imine containing) analogues. More specifically, catalyst **12-Ti** polymerized L-LA 1.2× faster than **1-Ti** ($k_{\text{obs}} = 0.31 \pm 0.02$ and $0.26 \pm 0.01 \text{ h}^{-1}$, respectively) and catalyst **12-Zr** polymerizing L-LA 3.3× faster than **1-Zr** ($k_{\text{obs}} = 8.6 \pm 0.9$ and $2.58 \pm 0.03 \text{ h}^{-1}$, respectively) (**Figure 3.4**). While we hypothesize that these differences in activity may be the result of changes in electronic communication through the ligand scaffold upon elimination of the imine moieties, we cannot discount the possibility that electronic perturbation of salan-derived catalysts **12-Ti** and **12-Zr** may also result due to the adoption of a different ligand coordination environment than of their salen-based analogues **1-Ti** and **1-Zr**. Such differences in coordination geometry have been shown by B. Long and coworkers to dramatically impact catalytic activity and redox-switchability, wherein catalysts adopting a β -cis geometry were shown to have completely opposite reactivity trends to those adopting either *trans* or α -cis configurations (**Scheme 3.3**).⁹¹ Such coordination geometry considerations may prove critical in this study, as many salen-type catalysts (such as **1**) typically adopt a *trans* configuration while salan-type catalysts (such as **12**) typically adopt an α -cis configuration.¹⁶⁶ Therefore, we anticipate that single-crystal X-ray diffraction studies may be required to confirm the geometric configurations of catalysts **1-Zr**, **12-Ti**, and **12-Zr**, which will then be used to inform future computational investigations into the

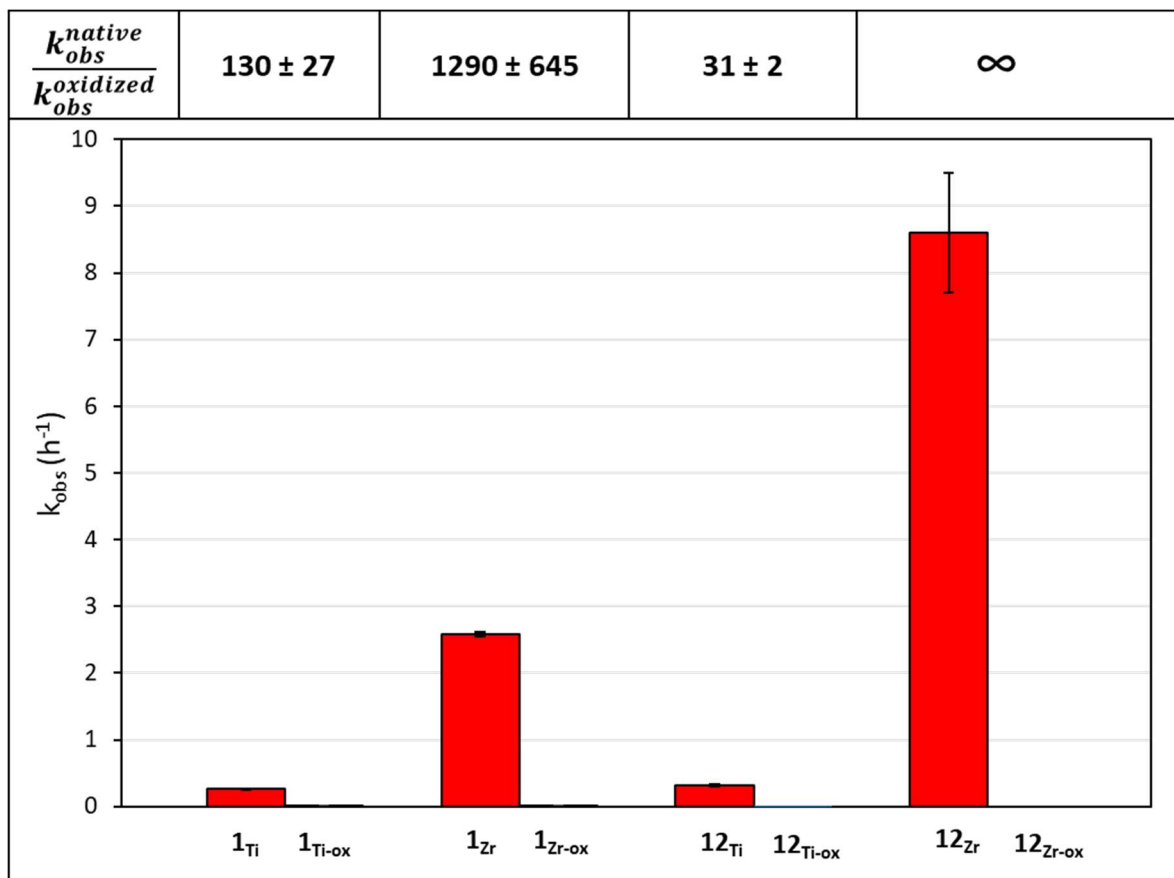
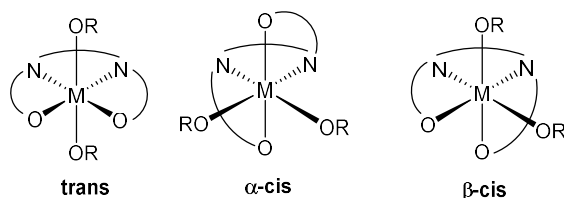


Figure 3.4 Comparison of k_{obs} for catalysts $1_{Ti}/1_{Ti-ox}$, $1_{Zr}/1_{Zr-ox}$, $12_{Ti}/12_{Ti-ox}$, and $12_{Zr}/12_{Zr-ox}$. Conditions: 10 μ mol catalyst, 0.7 mmol L-LA, 1 M in C_6D_6 , 90 °C.

mechanistic details of the observed L-LA polymerization behavior.

Scheme 3.3 Possible Geometric Configurations for [ONNO]-Type Catalysts



To investigate how changes in electronic communication through the ligand affects catalyst redox-switchability for the polymerization of L-LA, differentiation in polymerization activity between the native and oxidized states ($k_{obs}^{native}/k_{obs}^{oxidized}$) of catalysts bearing the same metal center were compared (**1_{Ti}** vs. **12_{Ti}** and **1_{Zr}** vs. **12_{Zr}**). Catalysts **1_{Ti}** and **12_{Ti}** were seen to have drastically different switching performances, yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of $130 (\pm 27)$ and $31 \pm (2)$, respectively. In contrast, catalysts **1_{Zr}** and **12_{Zr}** exhibited similar differentiation in polymerization activity between the native and oxidized states, yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of $1290 (\pm 645)$ and approaching infinity, respectively (**Figure 3.4**). In catalyst **1**, electronic communication from the ferrocenyl moieties to the metal center may occur through both the phenolic and imine moieties, whereas in catalyst **12** this electron transfer is isolated to the pathway through the phenolic moieties. We hypothesize that if electronic communication from the metal center is lessened via elimination of conjugation through the imine moieties, then the electrophilicity of the metal center may not increase as greatly, relative to that of the native catalyst. This may also lessen the stabilization of the five membered metallocycle intermediate compared to native catalyst, which could account for the significantly lower $k_{obs}^{native}/k_{obs}^{oxidized}$ ratio observed for **12_{Ti}** as compared to **1_{Ti}**.

To further investigate these catalysts, we also examined the polymerization of CL using **1_{Ti}**, **1_{Zr}**, **12_{Ti}** and **12_{Zr}** in their native, oxidized, and reduced ligand states. The CL ROP behavior of each catalyst was likewise monitored in C₆D₆ at 90 °C via ¹H NMR spectroscopy. Again, all catalysts were seen to be more active in the native Fe(II) state than in the oxidized Fe(III) state but with varying overall rates (**Figure 3.5**). Catalyst **1_{Ti}** was found to reach 90% conversion in approximately 6.5 h ($k_{obs} = 0.36 \pm 0.02 \text{ h}^{-1}$) (**Figure A.75**). In contrast, the oxidized catalyst **1_{Ti-ox}** reached only about 10% monomer conversion in the same period ($k_{obs} = 0.02 \pm 0.003 \text{ h}^{-1}$) (**Figure A.76**). The reduced form **1_{Ti-red}** polymerized CL with a slightly faster rate than **1_{Ti}** ($k_{obs} = 0.5 \pm 0.2 \text{ h}^{-1}$) (**Figure A.77**).

Conversely, catalyst **12_{Ti}** and **12_{Zr}** were found to be more active reaching 90% conversion in approximately 0.58 h ($k_{obs} = 4.41 \pm 0.01 \text{ h}^{-1}$) (**Figure A.81**) and 0.37 h ($k_{obs} = 6.2 \pm 0.2 \text{ h}^{-1}$) (**Figure A.84**), respectively. The oxidized catalysts **12_{Ti-ox}** and **12_{Zr-ox}** were slower taking 10 h ($k_{obs} = 0.09 \pm 0.03 \text{ h}^{-1}$) (**Figure A.82**) and 5 h ($k_{obs} = 0.14 \pm 0.02 \text{ h}^{-1}$) (**Figure A.85**), respectively, to reach 50% monomer conversion. Catalyst **12_{Ti-red}** polymerized CL with a rate similar to **12_{Ti}** reaching 90% conversion in 0.67 h ($k_{obs} = 3.5 \pm 0.5 \text{ h}^{-1}$) (**Figure A.83**). However, even though catalyst **12_{Zr-red}** was active for the polymerization of CL it exhibited a slower rate than **12_{Zr}** reaching 90% conversion in approximately 1.2 h ($k_{obs} = 2 \pm 1 \text{ h}^{-1}$) (**Figure A.86**). This decrease in polymerization rate is most likely due to incomplete reduction upon addition of CoCp₂ or partial catalyst decomposition upon oxidation and reduction, as was previously observed for catalyst **12_{Zr}**.

Catalyst **1_{Zr}** was found to be the most active reaching 90% conversion in only 0.2 h ($k_{obs} = 10.8 \pm 0.5 \text{ h}^{-1}$) (**Figure A.78**). Even though the oxidized form, **1_{Zr-ox}**, was found to be less active than the native catalyst it was significantly more active than the oxidized states of the other catalysts (**1_{Ti}**, **12_{Ti}**, and **12_{Zr}**) reaching 90% monomer

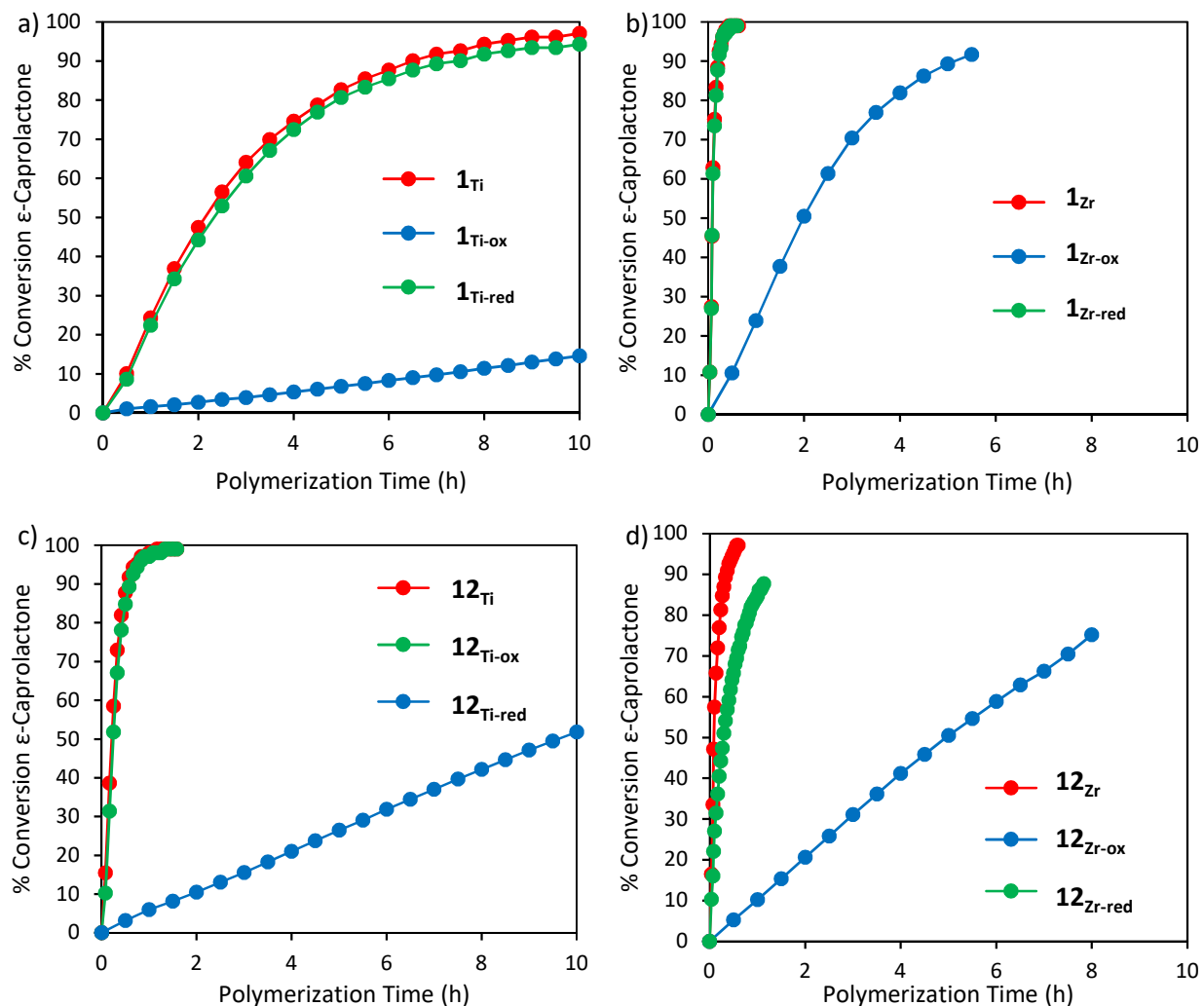
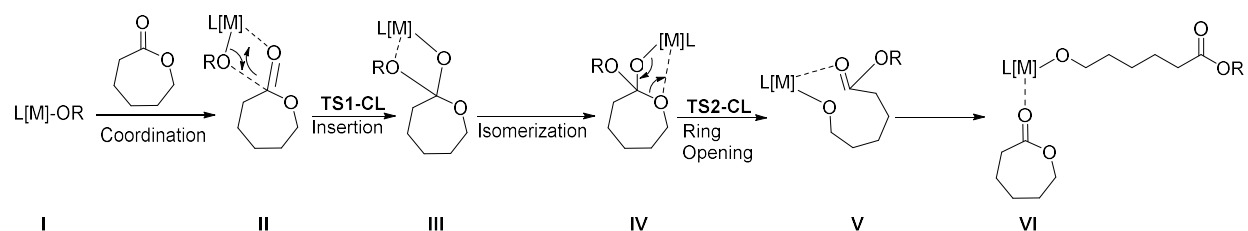


Figure 3.5 Plot of monomer conversion (%) versus time (h) for the polymerization of CL (100 eq, 1M) as determined by 1H NMR spectroscopy in C_6D_6 at 90 $^{\circ}C$ using (a) 1_{Ti} (red circles), 1_{Ti-ox} (blue circles), and 1_{Ti-red} (green circles), (b) 1_{Zr} (red circles), 1_{Zr-ox} (blue circles), and 1_{Zr-red} (green circles), (c) 12_{Ti} (red circles), 12_{Ti-ox} (blue circles), and 12_{Ti-red} (green circles), and (d) 12_{Zr} (red circles), 12_{Zr-ox} (blue circles), and 12_{Zr-red} (green circles). Using AgOTf as an oxidizing agent and CoCp₂ as a reducing agent.

conversion in 5 h ($k_{\text{obs}} = 0.48 \pm 0.04 \text{ h}^{-1}$) (**Figure A.79**). The reduced form **1_{Zr-red}** polymerized CL with a rate similar to **1_{Zr}** reaching 90% conversion in about 0.2 h ($k_{\text{obs}} = 10.0 \pm 0.9 \text{ h}^{-1}$) (**Figure A.80**).

The polymerization of CL with catalysts **1_{Ti}**, **1_{Zr}**, **12_{Ti}** and **12_{Zr}** occurs via the same coordination-insertion ROP mechanism as the polymerization of LA (**Scheme 3.4**); however, it has previously been shown by Diaconescu and colleagues that the RDS is different for each monomer.¹⁰³ During the polymerization of CL, the RDS has been calculated to be nucleophilic attack by the alkoxide ligand (**TS1**), whereas the RDS for the polymerization LA is the ring-opening step (**TS2**). This difference in RDS is hypothesized to be due to the higher ring strain of CL as compared to LA ($\Delta H_p = -29$ vs. -23 kJ/mol , respectively).⁹⁹ It should also be noted that after insertion of the first CL monomer, coordination of the carbonyl to the metal center forms a nine membered metallocycle intermediate (**V**) which is less stable than the five membered metallocycle intermediate formed during the polymerization of LA. Prior reports have suggested that formation of this less stable nine membered metallocycle intermediate leads to the faster overall rate of polymerization observed for CL, as compared to LA.¹⁰³

Scheme 3.4 Mechanism for the Coordination-Insertion ROP of CL



As previously discussed, oxidation of the ferrocenyl moieties decreases the electron density at the active metal center increasing the metal centers electrophilicity and strengthening coordination with the monomer carbonyl.^{94, 96, 103} This increase in electrophilicity as compared to the native catalyst also leads to a decrease in the nucleophilicity of the alkoxide ligand.¹⁰⁶ The combined effect of this strong monomer coordination and the weak nucleophilicity of the alkoxide are hypothesized to result in an increase in the overall energy barrier of CL polymerization as compared to the native catalyst making the polymerization thermodynamically less favorable after catalyst oxidation accounting for the lower activity observed experimentally.

Comparison of the k_{obs} values of each catalyst in the native state was again used to examine how ligand structure and metal center identity affect catalytic activity, while differentiation in polymerization activity between the native and oxidized catalyst state ($k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$) was used to examine how electronic communication through the ligand scaffold affects catalyst redox-switchability (**Figure 3.6**). As expected, Zr-based catalysts **1_{Zr}** and **12_{Zr}** exhibited higher activities for the ROP of CL than their Ti-based analogues, **1_{Ti}** and **12_{Ti}**, which agrees with our previous studies of Zr- vs. Ti-based catalysts.^{96, 98} When the native state activity of catalysts bearing the same metal center were compared, catalyst **12_{Ti}** polymerized CL 12.3× faster than **1_{Ti}** ($k_{\text{obs}} = 4.41 \pm 0.004$ and $0.36 \pm 0.02 \text{ h}^{-1}$, respectively) and catalyst **1_{Zr}** polymerized CL 1.7× faster than **12_{Zr}** ($k_{\text{obs}} = 10.8 \pm 0.5$ and $6.2 \pm 0.2 \text{ h}^{-1}$, respectively) (**Figure 3.6**). Moreover, both salan-type catalysts exhibited a greater differentiation in polymerization activity between the native and oxidized states than salen-type catalysts with **12_{Ti}** and **1_{Ti}** yielding $k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$ ratios of $49 \pm (16)$ and $36 (\pm 11)$, respectively, while **12_{Zr}** and **1_{Zr}** yielding $k_{\text{obs}}^{\text{native}}/k_{\text{obs}}^{\text{oxidized}}$ ratios of $44 (\pm 7)$ and $23 (\pm 3)$, respectively (**Figure 3.6**). As previously discussed, we hypothesize that these differences in activity and redox-

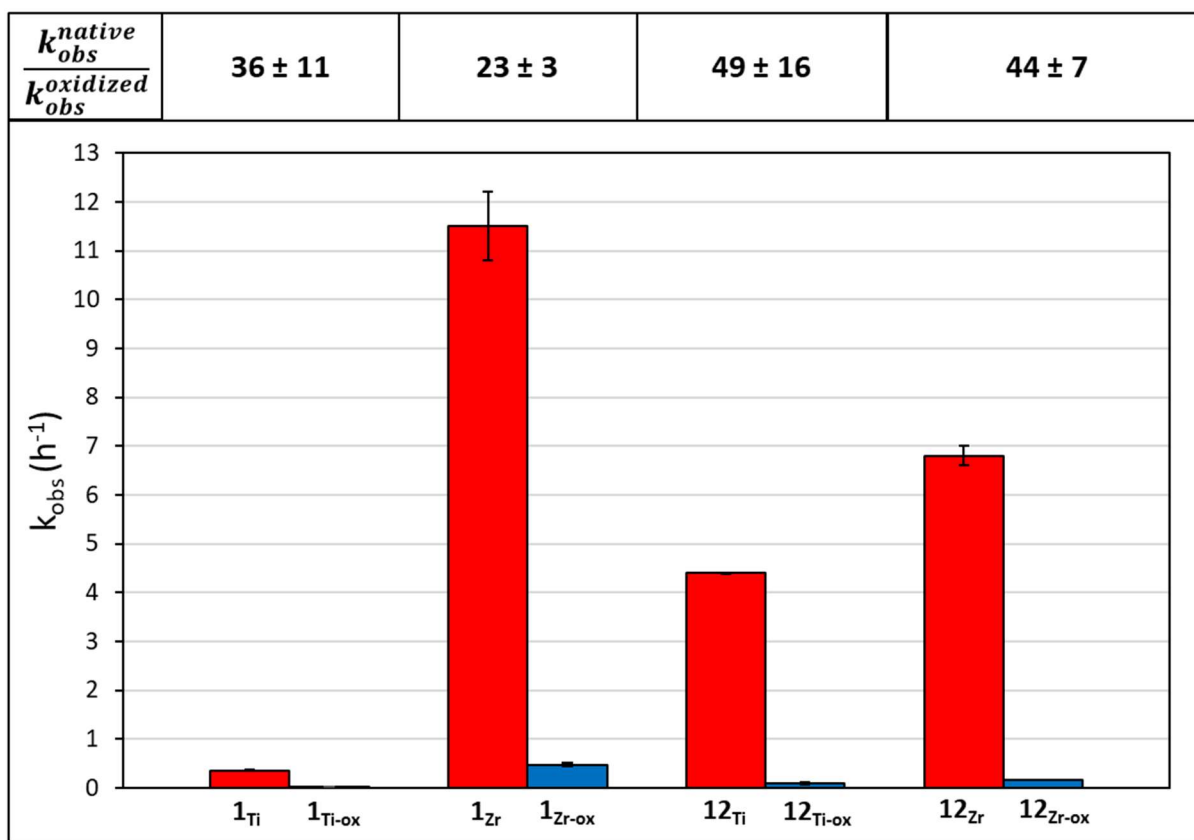


Figure 3.6 Comparison of k_{obs} for catalysts $1_{Ti}/1_{Ti-ox}$, $1_{Zr}/1_{Zr-ox}$, $12_{Ti}/12_{Ti-ox}$, and $12_{Zr}/12_{Zr-ox}$. Conditions: 10 μmol catalyst, 0.7 mmol CL, 1 M in C_6D_6 , 90 $^\circ\text{C}$.

switchability may be due to a change in the electronic communication and geometric configuration of salen- vs. salan-type catalysts.

3.3 Conclusion

In summary, we have investigated four Ti- and Zr-based redox-active [ONNO] catalysts to determine how the connectivity and conjugation of the ligand scaffold and the identity of the active metal center affect catalytic activity, selectivity, and overall redox-switchability for the ROP of L-LA and CL. Our results demonstrate that salen-type catalysts **1_{Ti}** and **1_{Zr}** and salan-type catalysts **12_{Ti}** and **12_{Zr}** are all active for the ROP of L-LA and CL in their native states and are significantly less active in their oxidized states. Additionally, in all cases the Zr-based catalysts (**1_{Zr}** and **12_{Zr}**) exhibited higher activities than their Ti-based analogues (**1_{Ti}** and **12_{Ti}**).

For the polymerization of L-LA, it was seen that both salan-type catalysts were more active than their salen-type analogues with catalyst **12_{Ti}** polymerizing L-LA 1.2× faster than **1_{Ti}** and catalyst **12_{Zr}** polymerizing L-LA 3.3× faster than **1_{Zr}**. Catalysts **1_{Ti}** and **12_{Ti}** were also seen to have drastically different switching performances, yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of $130 (\pm 27)$ and $31 (\pm 2)$, respectively. In contrast, catalysts **1_{Zr}** and **12_{Zr}** exhibited similar differentiation in polymerization activity between the native and oxidized states, yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of $1290 (\pm 645)$ and approaching infinity, respectively.

For the polymerization of CL, catalyst **12_{Ti}** was seen to catalyze **12_{Ti}** polymerized CL 12.3× faster than **1_{Ti}** and catalyst **1_{Zr}** polymerized CL 1.7× faster than **12_{Zr}**. Moreover, both salan-type catalysts exhibited a greater differentiation in polymerization activity between the native and oxidized states than salen-type catalysts with **12_{Ti}** and **1_{Ti}** yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of $49 (\pm 16)$ and $36 (\pm 11)$, respectively, while **12_{Zr}** and **1_{Zr}** yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of $44 (\pm 7)$ and $23 (\pm 3)$, respectively.

We hypothesize that as the architecture of the ligand is varied (salen vs. salan), the electronic communication through the ligand scaffold, as well as the geometric configuration of the catalyst, may be altered leading to the changes in catalytic activity, selectivity, and redox-switchability observed. However, the mechanistic rationale for these changes in catalytic behavior with modification of the connectivity and conjugation of the ligand scaffold are not fully understood at this time. Therefore, computational examination of the key transition states and intermediates involved in the initiation and propagation for the ROP of L-LA and CL using each catalyst (**1_{Ti}**, **1_{Zr}**, **12_{Ti}**, and **12_{Zr}**) could provide valuable insight and a deeper understanding of the experimentally observed changes in catalytic behavior. These investigations may be the subject of future investigations in the Long group.

Chapter 4 – Introduction to Olefin Polymerization Catalysis

4.1 Motivation

The consumer plastics industry is dominated by petroleum-based, synthetic polymers such as PE and PP.¹¹⁰⁻¹¹² The widespread usage of these polymers is due to their remarkable low cost and high thermal and mechanical properties. Furthermore, the microstructure and topology of PE can be tailored in order to tune the material's thermal and mechanical properties making PE attractive for a plethora of applications.¹⁷¹⁻¹⁸⁰ One method by which the topology of PE can be tailored is through the incorporation of long chain branches via the copolymerization of ethylene with higher α -olefins. However, while the incorporation of higher α -olefins is an effective method for tailoring the properties of the PE produced, these comonomers are produced via the oligomerization of ethylene resulting in a significant increase in the cost of producing these materials. Therefore, another method by which PE topology can be varied that does not lead to a significant increase in the cost of production is highly sought after.

One method by which this can be accomplished is through the use of late transition metal-based catalysts which can produce branched PE using ethylene as the sole feedstock. Therein, branched PE is produced due to the propensity of late transition metal-based catalysts to migrate along the growing polymer chain via a process known as "chain-walking."^{181, 182} Furthermore, it has been shown that the topology of the PE obtained with these catalysts can be tuned via changes in polymerization conditions such as polymerization pressure¹⁸² and temperature,¹⁸³ as well as through modification to the ligand's structure such as heteroatom connection, backbone identity, steric effects and electronic effects.^{184, 185} Herein, we will discuss the developments within the field of PE catalysis that have influenced our studies into late transition metal-based catalysts for the polymerization of ethylene with tunable polymer topologies.

4.2 Early Polymerization Catalysts

During the 1950s, the first major discoveries of ethylene polymerization catalysts were made with the independent development of two heterogeneous transition metal catalysts- TiCl_4 by Karl Ziegler and Giulio Natta^{186, 187} and Cr_2O_3 by J. Paul Hogan and Robert L. Banks (**Figure 4.1**).¹⁸⁸ In 1951 Hogan and Banks' Cr_2O_3 catalyst system was shown to produce PP as well as high density PE (HDPE); ultimately earning them a patent for Phillips Petroleum Company.¹⁸⁸ Around the same time, Ziegler and Natta's TiCl_4 catalyst system was shown to produce isotactic PP and HDPE, resulting in them receiving the Nobel Prize in 1963.¹⁸⁹ To this day, both of these heterogeneous catalysts are used industrially with Hogan and Banks' Cr_2O_3 catalyst accounting for most of the worldwide production of HDPE.¹⁸⁸ Although these catalysts are industrially intriguing and relevant, their mechanistic details are less well known due to complications involved with studying heterogeneous systems. The main complication of heterogeneous systems is that they possess multiple active sites that can vary in activity, reactivity, and selectivity making it difficult to gain fundamental insight into the polymerization activity of these systems. Therefore, the academic community has focused more heavily on the development and design of homogeneous, single-site catalysts.

Early exploration into homogeneous, single-site catalysts for the polymerization of α -olefins was focused on the development of group IV metallocenes. The study of metallocenes remained largely dormant until the discovery of methylaluminoxane (MAO) in the early 1980's by Kaminsky and colleagues.¹⁹⁰ Metallocenes were seen to be highly active for the polymerization of ethylene when using MAO as a cocatalyst resulting in the almost exclusive formation of HDPE unless ethylene was copolymerized with higher α -olefins (**Scheme 4.1**). Due to the

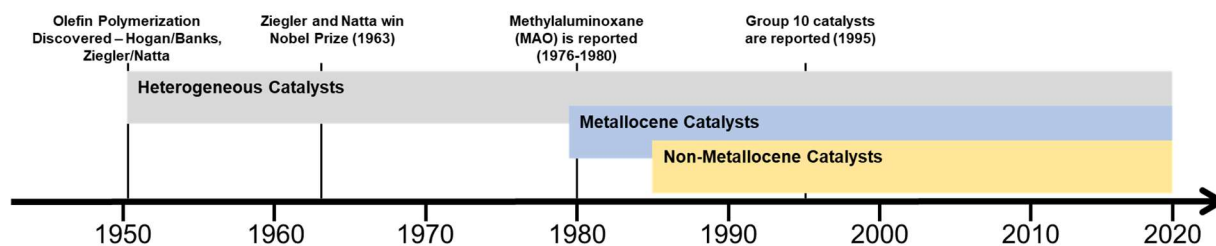
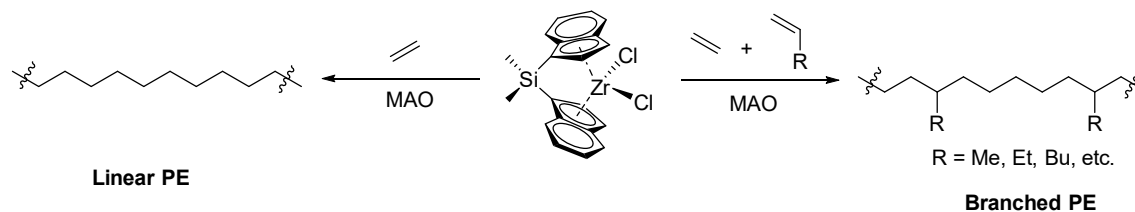


Figure 4.1 Timeline of olefin polymerization catalysts development.

Scheme 4.1 Early group IV centered metallocene catalyst that can be used to produce linear PE when using ethylene as the sole feedstock or branched PE when using ethylene and a higher α -olefin as the feedstock



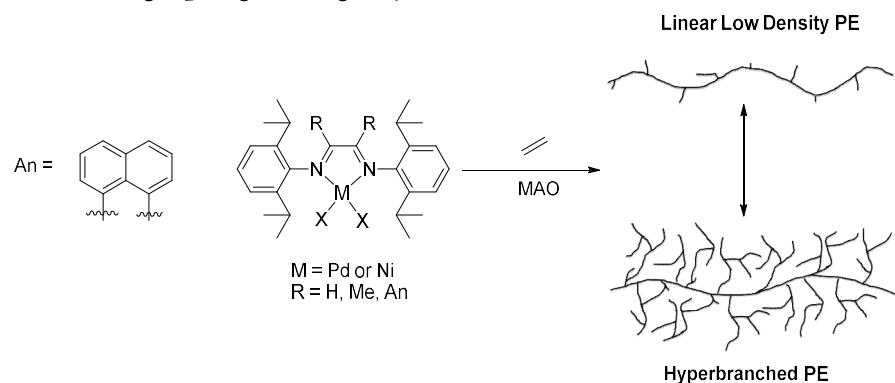
versatility of MAO as a cocatalyst researchers were able to not only access myriad highly active metallocene catalysts but were able to expand their exploration to alternative, non-metallocene ligand scaffolds as well.^{184, 191, 192}

4.3 Late Transition Metal-Based Catalysts for the Polymerization of Ethylene

4.3.1 Development of α -Diimine Ni- and Pd-Based Catalysts

In 1995, one of the first late transition metal-based catalysts was reported by Brookhart and co-workers.^{185, 193} Utilizing an α -diimine ligand scaffold, they demonstrated that late transition metal-based catalysts, namely Ni and Pd, could be used to produce high molecular weight, branched PE using ethylene as the sole feedstock. The results of the work led to the extensive development and study of group 10 centered polymerization catalysts as they offer a means by which PE with a variety of topologies can be accessed without the use of more expensive α -olefin comonomers (**Scheme 4.2**). The ability of these group 10 centered catalysts to produce PE with a variety of branching structures was found to be the result of a process known as “chain-walking.”^{181, 182} Chain-walking occurs due to a catalyst’s propensity to undergo β -hydride elimination and subsequent reinsertion (**Figure 4.2**). As this process is repeated throughout the polymerization, it allows the active catalyst to “walk” along the polymer backbone. Consequently, if a molecule of ethylene coordinates to the active metal center and inserts during this process, a branch point is created on the polymer backbone. The discovery of the chain-walking process led researchers to show that the topology of PE produced with these group 10 centered α -diimine catalysts can be tuned via changes to polymerization conditions and through modification of the ligand structure.¹⁸²⁻¹⁸⁵

Scheme 4.2 Representative group 10 centered non-metallocene catalyst that can produce PE with a variety of branching topologies using ethylene as the sole feedstock



4.3.2 Modulation of Polymer Topology with Group 10 Centered α -Diimine Catalysts

In 1999, Guan and coworkers showed that PE branching topology could be modulated as a function of ethylene pressure.¹⁸² When ethylene pressures were increased, more linear PE with shorter branches was produced, whereas decreased ethylene pressures result in more highly branched materials (**Figure 4.3a** and **b**). This change in branching topology with changes in ethylene pressure were attributed to changes in the ratio of ethylene coordination and insertion relative to that of β -hydride elimination and reinsertions. Therein, when a higher ethylene pressure is used during polymerization, the concentration of ethylene is increased resulting in an increase in the occurrence of ethylene coordination and insertion relative to that of β -hydride elimination and reinsertion. In contrast, when a lower ethylene pressure is used during polymerization, the concentration of ethylene is

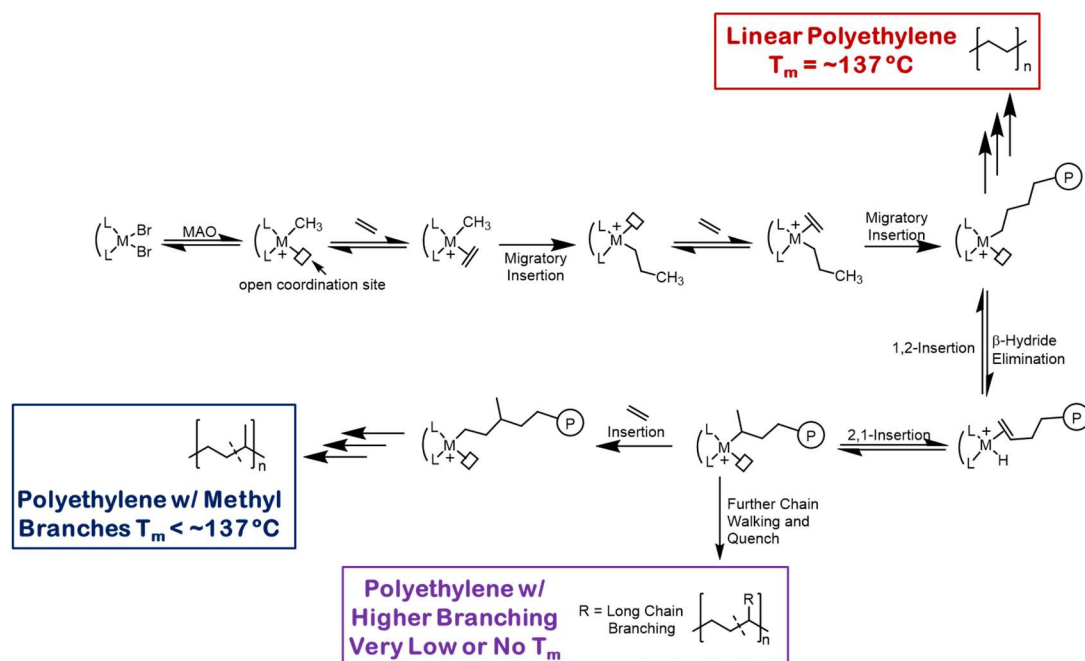


Figure 4.2 Polymerization of ethylene via a chain-walking mechanism.

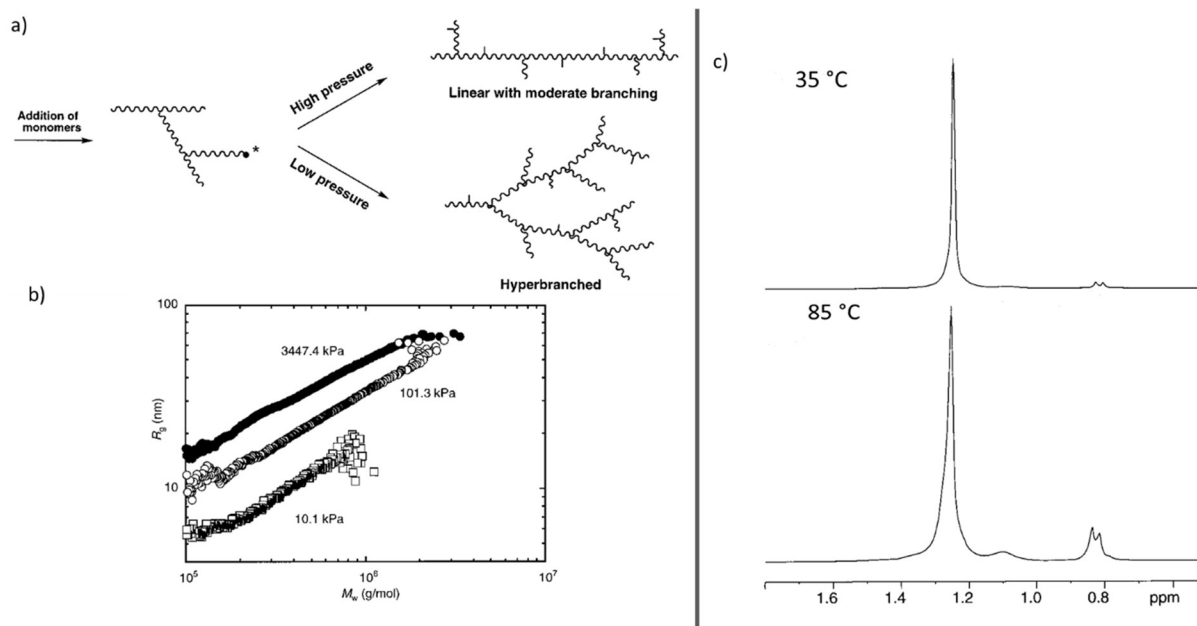


Figure 4.3 a) Representations of the variation in PE branching density with changes in pressure. b) Logarithmic plot of PE radius of gyration (R_g) vs. molecular weight (M_w) for PE obtained using a Pd-based α -diimine catalyst. Reprinted with permission from *Science*, **1999**, 283, 2059. Copyright 1999 AAAS. c) Representation of the variation in PE branching density with changes in temperature as measured by NMR spectroscopy. Reprinted with permission from *Macromolecules* **2000**, 33, 2320-2334. Copyright 2000 American Chemical Society.

decreased resulting in a decrease in the occurrence of ethylene coordination and insertion relative to that of β -hydride elimination and reinsertion (**Figure 4.2**). Additionally, in 2000 Brookhart and colleagues found that changes in polymerization temperature could be used to modulate PE branching topology.¹⁸³ They found that as the temperature of polymerization was increased from 35 °C to 85 °C the branching density of the PE produced increased as is evident by the increase in the methyl proton peak integration at approximately 0.8 ppm (**Figure 4.3c**). This change in branching topology was also attributed to changes in the ratio of ethylene coordination and insertion relative to that of β -hydride elimination and reinsertions. As the temperature of polymerization is increased less ethylene is solubilized within the polymerization solvent therefore decreasing the concentration of ethylene and the occurrence of coordination and insertion relative to that of β -hydride elimination and reinsertions (**Figure 4.2**).

Researchers have also explored variation of the ligand scaffold as a means to tune the topology of the PE obtained. To this end, researchers have probed how changes to the identity of the α -diimine backbones, heteroatom connectivity, steric constraints, and electronic nature of the ligand scaffold affect catalytic activity and polymer topology.^{184, 185} We are interested in how changes in ligand electronics affect polymer topology. When the electronic nature of the ligand is varied, so too is the electron density at the active metal center which is hypothesized to result in changes to the relative rates of monomer coordination and insertion as compared to β -hydride elimination and reinsertions.¹⁹⁴⁻¹⁹⁷ One of the first examples of this was reported by Guan and colleagues in 2005, who studied a series of Pd-based α -diimine catalysts bearing a variety of EW or ED *N*-aryl substituents.¹⁹⁴

Guan and coworkers showed that inclusion of ED substituents onto the *N*-aryl moieties of the catalyst resulted in the production of PE with a more linear structure whereas inclusion of EW substituents onto the catalyst resulted in the production of PE with a more highly branched structure (**Figure 4.4**). The authors hypothesized that this change in branching content arises due to changes in the σ -donating ability of the ligand, which in turn alters the Lewis acidity of the active metal center and the relative rate of chain-walking to that of coordination and insertion.^{194, 195, 198, 199} For example, when an EW substituent is introduced to the ligand scaffold electron density is believed to be withdrawn from the d-orbital of Pd that is involved in overlap with the filled σ -orbital of C $_{\beta}$ -H $_{\beta}$ which would strengthen the β -agostic interaction resulting in an increase in PE branching topology. However, validity of this mechanistic rationale was not examined further.

Following this seminal report, other researchers have reported on how the presence of EW or ED substituents on either the *N*-aryl moieties^{174, 194, 200-206} or the backbone²⁰⁷⁻²⁰⁹ of Ni- and Pd-based α -diimine catalysts affects the catalytic activity and polymer topology. However, to the best of our knowledge, there have been no studies conducted to systematically investigate how substituent identity and placement on Ni- or Pd-based α -diimine catalysts affect PE branching topology. Furthermore, we noted that the trends observed in most prior studies^{174, 194, 200-209} were determined experimentally, requiring the synthesis of multiple discrete catalyst species, as well as exhaustive polymerization studies. Therefore, we envision that if PE branching topology could be predicted based upon catalyst structure or an intrinsic catalyst characteristic, without requiring extensive polymerization studies, that the selection and design of future catalytic species may be accelerated.

4.4 Research Objectives

The overall objective of Chapter 5 is to systematically study how changes in substituent identity and placement on the ligand scaffold affect the catalytic activity and resulting polymer topology during the

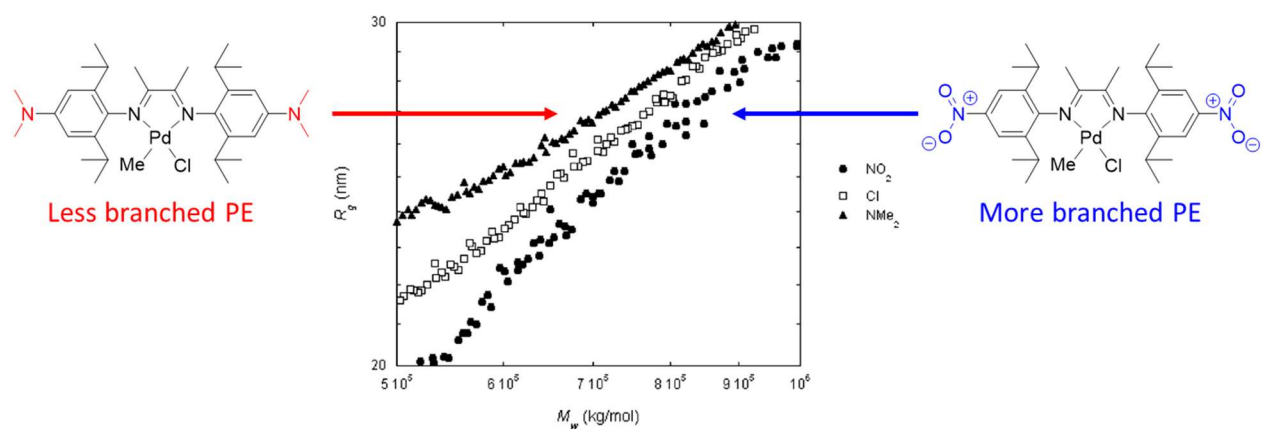


Figure 4.4 Logarithmic plot of PE radius of gyration (R_g) vs. molecular weight (M_n) for PE obtained using NO_2 , Cl , and NMe_2 substituted α -diimine catalysts with Pd-metal centers. Adapted with permission from *Organometallics*, **2005**, *24*, 1145-1155. Copyright 2005 American Chemical Society.

coordination-insertion polymerization of α -olefins. In particular, we will examine how the placement of EW and ED substituents on either the acenaphthene backbone, the *N*-aryl moieties, or both the acenaphthene backbone and *N*-aryl moieties of Ni-based α -diimine catalysts affect PE branching density as compared to the unsubstituted variant (**Figure 4.5**). Furthermore, because placement of EW and ED groups are anticipated to alter the electronic nature of the catalyst, we hypothesize that the catalysts' electrochemical reduction potential may be leveraged to provide a direct correlation to branching density. The scope of this project includes:

- I. Design, synthesis, and characterization (^1H and ^{13}C NMR spectroscopy and mass spectrometry) of α -diimine type ligands with acenaphthene derived backbone and a variety of electron-withdrawing or electron-donating substituents, as well as their Ni-based catalysts
- II. Polymerization of ethylene and examination of PE branching density using ^1H NMR spectroscopy and characterization via GPC and differential scanning calorimetry (DSC)
- III. Determination of catalyst reduction potential ($E_{1/2}$) and generation of a calibration curve by leveraging the correlation between PE branching density and catalyst $E_{1/2}$
- IV. Utilization of the above-mentioned calibration curve to predict the PE branching density obtained from a variety of other Ni-based α -diimine catalysts

The main purpose of Chapter 5 is to study the effects that systematic changes to the ligand scaffold of group 10 α -diimine catalysts have on PE branching topology. The results of this study will provide fundamental insight into the design of group 10 catalysts for the formation of PE with a variety of branching densities. Specifically, we will work to determine how substituent identity (EW vs. ED substituents) and placement (backbone vs. *N*-aryl moieties) on the ligand scaffold affect the polymer branching density of Ni-based acenaphthene derived α -diimine catalysts for the polymerization of ethylene. Furthermore, we will generate a calibration curve by leveraging the relationship between catalyst $E_{1/2}$ and PE branching density, which can be used to predict the PE branching density of Ni-based acenaphthene derived α -diimine catalysts without the need for extensive polymerization studies.

In Chapter 5, a library of new Ni-based α -diimine catalysts were synthesized to examine the effect that identity and placement of EW and ED substituents had on the branching density of the PE produced. To study the effect of these factors, six new Ni-based acenaphthene derived α -diimine catalysts bearing either EW nitro or ED methoxy substituent(s) were tested for the polymerization of ethylene and the PE branching density of each was compared to that obtained for the unsubstituted variant. The synthesis, characterization, and polymerization behavior of each catalyst will be discussed in detail. Through comparison of these catalysts, we show that inclusion of EW nitro substituent(s) resulted in a decrease in the branching density of the PE produced. Conversely, inclusion of ED methoxy substituent(s) resulted in no change or a slight increase in the PE branching density. Furthermore, it was found that when the PE branching density was plotted against the catalysts' $E_{1/2}$ a linear trend emerged which could be leveraged to predict the branching density of other Ni-based acenaphthene derived α -diimine catalysts with EW (halide or nitro) or ED (methyl) substituents.

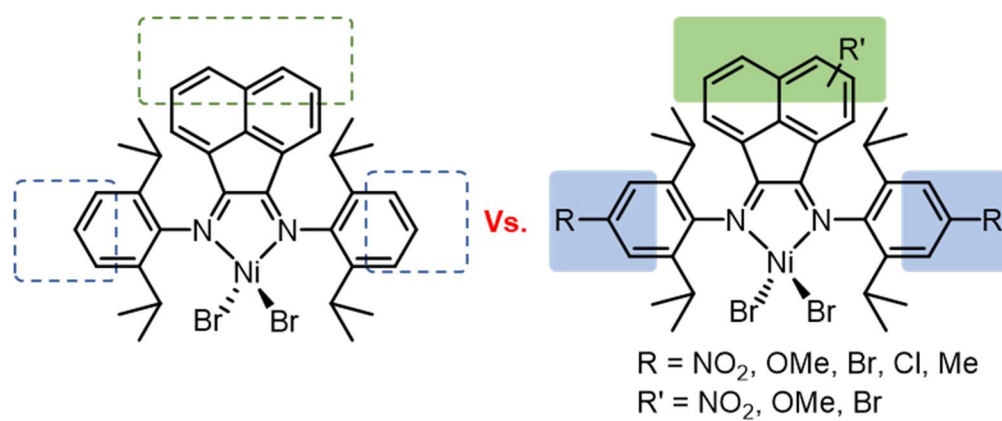


Figure 4.5 Representation of the catalysts developed in Chapter 5 to study the effect that substituent identity and placement on the ligand scaffold of acenaphthene derived α -diimine catalysts has on catalytic activity and branching density for the polymerization of ethylene.

Chapter 5 – Redox Potential of Nickel α -Diimine Catalysts as a Predictor of Polyethylene Branching Density

A version of this chapter has been submitted to a peer-reviewed journal by Alicia M. Doerr, Matthew R. Curry, Robert C. Chapleski, Justin M. Burroughs, Elizabeth K. Lander, Sharani Roy, and Brian K. Long and is currently under review.

Alicia M. Doerr, Matthew R. Curry, Robert C. Chapleski, Justin M. Burroughs, Elizabeth K. Lander, Sharani Roy, and Brian K. Long. “Redox Potential as a Predictor of Polyethylene Branching Density using Nickel α -Diimine Catalysts”

I performed the ligand and catalyst synthesis and characterization presented within this work. I also performed all polymerizations discussed, as well as writing most of the document. Matthew R. Curry, Dr. Robert C. Chapleski, Elizabeth K. Lander, and Dr. Sharani Roy performed the computational work presented within this work. Justin Burroughs obtained and analyzed all X-ray crystallographic data provided. Dr. Brian Long and Dr. Sharani Roy advised this work.

5.1 Introduction

The production of consumer plastics is dominated by synthetic, petroleum-based polymers, such as polyolefins that are produced on the scale of billions of pounds annually.²¹⁰ The widespread usage of polyolefins stems from their remarkably low cost and exceptional thermomechanical properties that may be fine-tuned via precise control over their microstructure and topology. These features ensure that polyolefin-based materials are attractive candidates for a plethora of applications.¹⁷¹⁻¹⁸⁰

A polyolefin of particular interest to this study is PE, which is routinely synthesized using heterogeneous or homogeneous transition metal catalysts via a coordination-insertion polymerization mechanism. When early transition metal-based catalysts are used, such as those containing Ti, Zr, or Hf, the microstructure and thermomechanical properties of the resultant PE may be altered via copolymerization of ethylene and higher α -olefins. However, reports by Brookhart and coworkers demonstrated that Ni- and Pd-based α -diimine catalysts could produce high molecular weight, branched PE using ethylene as the sole monomeric feedstock.^{185, 193} Therein, PE branching occurs due to the propensity of these Ni- and Pd-based catalysts to migrate along the growing polymer chain via a process known as “chain-walking.”^{181, 182}

Following these seminal reports of Ni- and Pd-based α -diimine catalysts, multiple methods to modulate PE topology have been reported.¹⁸²⁻¹⁸⁵ For example, Guan and coworkers found that PE branching could be modulated as a function of ethylene pressure when using Pd-based α -diimine catalysts. Therein, polymerizations ran under high ethylene feed pressures resulted in more linear PE, whereas low ethylene pressures resulted in more highly branched materials. This difference in branching was attributed to the relative ratios of ethylene coordination and insertion to that of β -hydride elimination and reinsertion (chain-walking).¹⁸² Alternatively, Brookhart and coworkers found that changes in polymerization temperature could similarly modulate branching density in which elevated reaction temperatures produce PE with increased branching density.¹⁸³

In addition to changes in reaction parameters (e.g. ethylene feed pressure and reaction temperature), changes in α -diimine ligand structure have also been shown to influence the degree of resultant PE branching. Changes in α -diimine ligand structure that have been studied include α -diimine backbone identity,^{184, 185, 209} as well as steric^{174, 184, 185, 205, 211-214} and electronic effects.^{174, 184, 185, 194, 196-208, 215-220} Salient examples include studies by Guan and coworkers who showed that placement of EW substituents on the *N*-aryl moieties of Pd-based α -diimines (**Figure**

5.1a) produced higher degrees of PE branching, whereas catalysts bearing ED substituents produce more linear PE under identical polymerization conditions.¹⁹⁴ The authors hypothesized that this change in branching content arises due to changes in the σ -donating ability of the ligand, which in turn alters the electron-density at the active metal center and the relative rate of chain-walking to that of coordination and insertion.^{194, 195, 198, 199} For example, when an EW substituent is introduced to the ligand scaffold, electron-density would be withdrawn from the d-orbital of Pd that overlaps with the filled σ -orbital of C β -H β . This strengthens the β -agostic interaction resulting in a greater propensity of the catalyst to undergo β -hydride elimination and an increase in PE branching topology is observed. However, validity of this mechanistic rationale was not examined further.

Chen and coworkers have also shown that placement of ED methoxy (-OMe) substituents on the acenaphthene backbone moiety of Pd- and Ni-based α -diimine catalysts may also influence PE branching (**Figure 5.1b**). More specifically, Ni-based catalysts bearing -OMe substituents produced PE with increased branching density as compared to their unsubstituted analogue under identical polymerization conditions. Conversely, Pd-based catalysts bearing -OMe substituents produced only a negligible decrease in PE branching density as compared to the unsubstituted analogue.²⁰⁸ However, the mechanistic details of these polymerizations and the resulting differences in PE topology were not well understood at the time.

Though the above-mentioned reports provide insight into the relationship between ligand-based electronic perturbations and polymerization behavior, several fundamental gaps remain. First, comprehensive studies designed to elucidate the relationship between ligand-based electronic modifications of Ni-based α -diimine catalysts (both EW and ED substituents) and PE branching density have not been reported. Second, systematic studies comparing placement of EW and ED substituents on the acenaphthene backbone versus placement of those same substituents on the *N*-aryl moieties of α -diimine ligands are absent from the literature. Lastly, we noted that the trends observed in most prior studies^{174, 194, 200-209} were determined experimentally, requiring the iterative synthesis of multiple discrete catalyst and ligand species, as well as extensive polymerization studies. However, we envisioned that if PE branching density could be predicted based upon catalyst structure or intrinsic catalyst and/or ligand characteristics, without requiring extensive polymerization studies and/or catalyst syntheses, that the selection and design of future catalytic species may be accelerated.

To address these issues, we herein experimentally and computationally elucidate the relationship between PE branching density and placement of EW or ED substituents about the a) acenaphthene backbone, b) *N*-aryl moieties, and c) both acenaphthene backbone and *N*-aryl moieties of Ni-based α -diimine catalysts. These results were compared to those obtained using the prototypical unsubstituted Ni α -diimine catalyst **13** (**Figure 5.2**). We will demonstrate that as ligand substituent placement and identity are varied, so too is the reduction potential ($E_{1/2}$) of the catalyst, revealing a strong linear relationship between catalyst $E_{1/2}$ and PE branching density. These experimental results agree well with computational results obtained in parallel and were used to generate a calibration curve relating PE branching to catalyst $E_{1/2}$. Finally, we will demonstrate that this calibration curve can be used to predict the PE branching density produced for other unique, substituted Ni-based α -diimine catalysts without the need to conduct extensive polymerization studies.

5.2 Results and Discussion

Unsubstituted and substituted acenaphthoquinone and aniline synthons were either purchased from commercial sources or synthesized according to modified literature procedures.^{208, 221-226} Unexpectedly, the

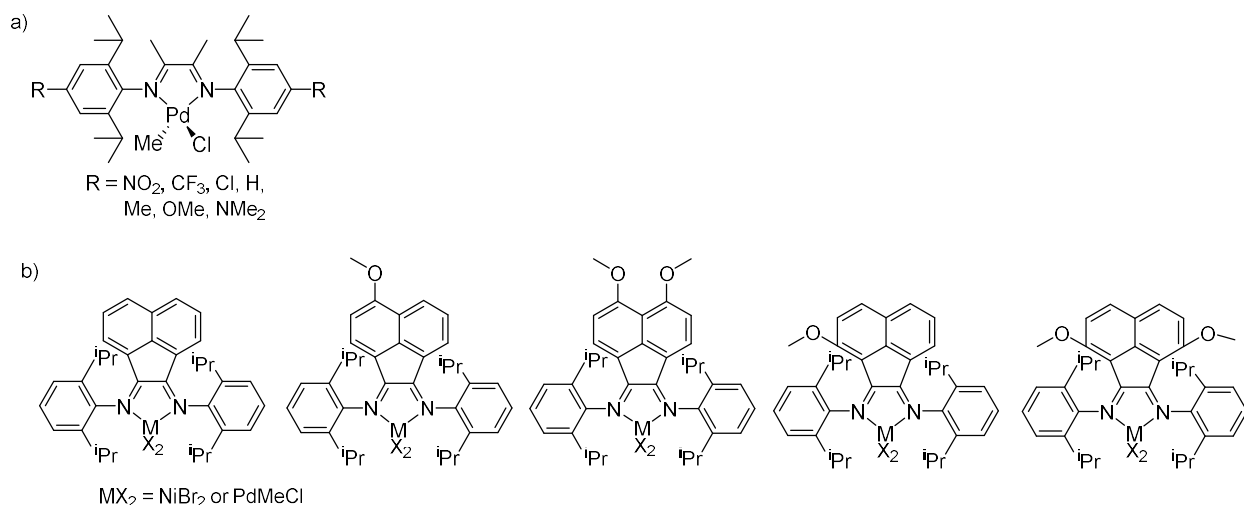


Figure 5.1 Structures of (a) Pd-based α -diimine catalysts bearing EW and ED substituents on the *N*-aryl moiety and (b) Ni- and Pd-based α -diimine catalysts bearing ED substituents on the acenaphthene backbone.

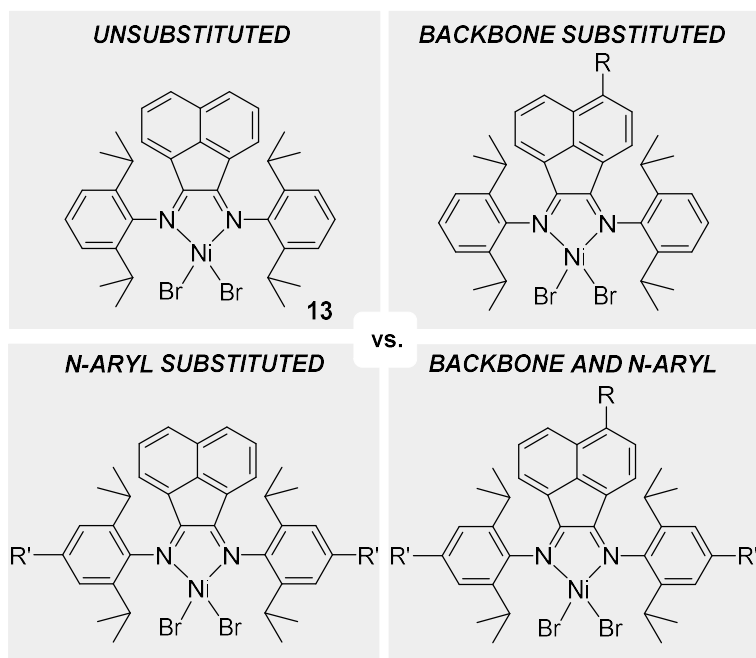
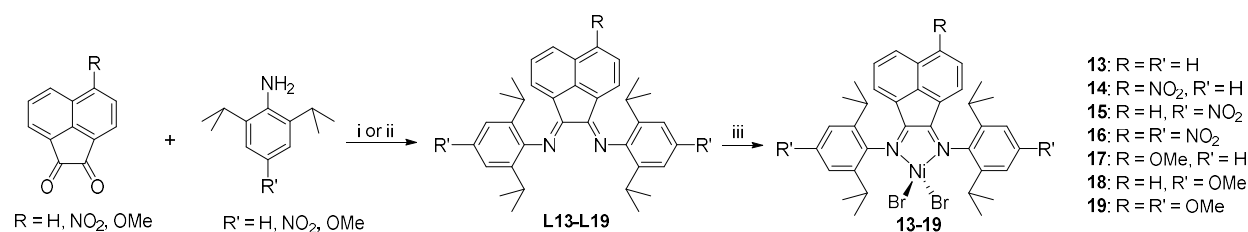


Figure 5.2 Unsubstituted Ni-based α -diimine catalyst **13** as compared to Ni-based α -diimine derivatives bearing EW/ED substituents on either the acenaphthene backbone, the *N*-aryl moieties, or on both the acenaphthene backbone and *N*-aryl moieties.

nitration of acenaphthoquinone using HNO_3 in H_2SO_4 yielded a mixture of the 5-nitroacenaphthoquinone and 4-nitroacenaphthoquinone isomers (**Figure 5.3**) though prior reports of this synthetic procedure did not discuss the formation or separation of a mixture of isomers.²²³⁻²²⁶ The two nitrated isomers were readily separated via silica gel flash column chromatography to yield pure 5-nitroacenaphthoquinone, which was used for subsequent studies. Ligands **L13-L19** (**Scheme 5.1**) were either obtained via condensation of substituted anilines with corresponding acenaphthoquinone derivatives using either formic acid in methanol (**L13**, **L14**, **L17**, **L19**), or by refluxing in toluene with catalytic p-toluene sulfonic acid in a Soxhlet extractor containing 4Å molecular sieves (**L15**, **L16**, **L18**).^{193, 223-226}

Scheme 5.1 Synthesis of Catalysts 13-19. i) formic acid, MeOH, Δ ; ii) p-toluene sulfonic acid, toluene, Δ ; iii) $\text{Ni}(\text{DME})\text{Br}_2$, DCM (See Appendix A.5)



Ligands **L13-L19** were metallated using $\text{Ni}(\text{DME})\text{Br}_2$ to produce catalysts **13-19**, respectively, following previous literature procedures.¹⁹⁶ Catalysts **13-19** were characterized using standard analytical techniques and the structures of complexes **14**, **17**, and **19** were confirmed by single-crystal X-ray diffraction. Crystallographic quality crystals of **14** and **19** were produced via slow vapor diffusion of pentane into a saturated DCM solution, whereas complex **17** was crystallized by layering DCM with pentane. X-ray analysis revealed that catalysts **14** and **19** were dimeric in the solid state, as has been observed for other α -diimine catalysts.^{193, 196} Conversely, **17** was monomeric in the solid state and adopts a tetrahedral geometry about the Ni-center (**Figures A.150-A.152**). Numerous attempts were made to produce X-ray crystallographic quality crystals of catalysts **15-16** and **18**, though we were ultimately unsuccessful.

The ethylene polymerization activities of catalysts **13-19** were evaluated under a constant ethylene feed (15 psi) using PMAO-IP as an activator (**Table 5.1**). All catalysts were active for the polymerization of ethylene, yielding 1.1-2.6 g of PE with molecular weights ranging from $M_n = 104,000$ -239,000 g/mol and dispersities from $\mathcal{D} = 1.32$ -2.81. PE branching densities were measured via ^1H NMR spectroscopic analysis,²²⁷ wherein prototypical unsubstituted catalyst **13** yielded PE with 106 (± 2) branches/1000 carbons. In contrast, catalyst **14**, which incorporates an EW nitro substituent onto the acenaphthene backbone, produced PE with 66 (± 2) branches/1000 carbons. Placement of EW nitro substituents on the *N*-aryl moieties (**15**) and both the acenaphthene backbone and the *N*-aryl moieties (**16**) further decreased the PE branching density to 43 (± 3) and 49 (± 2) branches/1000 carbons, respectively.

The significant decrease in PE branching density observed for nitro-substituted catalysts **14-16** suggests that inclusion of EW substituents onto the α -diimine ligand scaffold generally decreases the rate of β -hydride elimination relative to that of subsequent ethylene coordination and insertion, as compared to the unsubstituted catalyst **13**. We believe that this change in the rate of β -hydride elimination is the result of changes to the strength

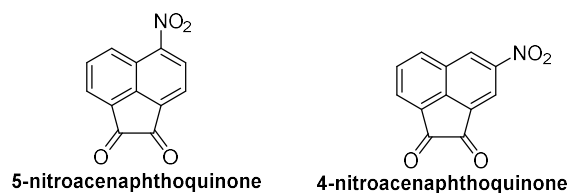


Figure 5.3 Mixture of isomers obtained during the nitration of acenaphthenequinone using HNO₃ and H₂SO₄.

Table 5.1 Polymerization of Ethylene Using Catalysts **13-19**.^a

Catalyst	Yield (g)	M _n ^b (kg/mol)	<i>D</i> ^b	B ^c	E _{1/2} (V)
13	2.6	104	1.91	106 (± 2)	-0.90
14	2.2	168	2.81	66 (± 2)	-0.64
15	1.4	239	2.59	43 (± 3)	-0.61
16	1.1	239	2.76	49 (± 2)	----- ^d
17	1.6	211	1.32	109 (± 1)	-0.94
18	2.2	239	1.68	102 (± 3)	-0.86
19	1.6	189	1.70	115 (± 1)	-0.99

^aPolymerization Conditions: 15 psi ethylene, 0.01 mmol catalyst, 0.92 mmol PMAO-IP, 148 mL toluene, 2 mL DCM, 30 min. ^bDetermined using triple detection gel permeation chromatography at 140 °C in 1,2,4-trichlorobenzene. ^cBranches/1000 carbons, determined by ¹H NMR at 100 °C in C₂D₂Cl₄,²²⁷ values are reported as averages over multiple polymerization trials and error is reported as one standard deviation.

of the β -agostic interaction. This interaction is comprised of σ -donation from a filled $C_{\beta}-H_{\beta}$ σ orbital of ethylene to an empty d-orbital on the metal center, as well as π -backbonding from a filled d-orbital on the metal center to the empty $C_{\beta}-H_{\beta}$ σ^*_{2p} orbital of ethylene. Therefore, we hypothesize that this difference in PE branching density arises from the π -withdrawing nature of nitro substituents, which withdraws electron-density from the filled d-orbital at the Ni-center. This withdrawal of electron-density from Ni results in a decrease in π -backbonding with the empty $C_{\beta}-H_{\beta}$ σ^*_{2p} of ethylene. This weakens the β -agostic interaction, decreases the likelihood of β -hydride elimination, and decreases PE branching density.

Conversely, incorporating methoxy substituents onto the acenaphthene backbone (**17**) and onto both the backbone and *N*-aryl moieties (**19**) marginally increased PE branching density to 109 (± 1) and 115 (± 1) branches/1000 carbons, respectively. Catalyst **18**, which features methoxy substituted *N*-aryl moieties produced slightly fewer branches (102 (± 3) branches/1000 carbons) than **13**. Though these results are outside of experimental error, they suggest that the electron density around the active Ni-center and therefore the rate of β -hydride elimination, relative to the overall rate of ethylene coordination and insertion, is similar for catalysts **13**, **17** and **18** and is only slightly increased for **19**. This increase is believed to arise due to the π -donating nature of methoxy substituents, which donates electron-density to the filled d-orbital at the Ni-center, increasing π -backbonding with the empty $C_{\beta}-H_{\beta}$ σ^*_{2p} of ethylene, strengthening the β -agostic interaction, increasing the likelihood of β -hydride elimination, and increasing PE branching density.

Having established general trends relating ED/EW group placement to PE branching density, we then sought to determine if an intrinsic catalyst characteristic could be leveraged so as to predict PE branching density without requiring extensive polymerization studies. For example, the effects of EW and ED substituents on the reactivity or selectivity of aromatic compounds are commonly expressed using quantitative structure-activity relationships, such as the Hammett equation.²²⁸ When PE branching densities obtained using catalysts **13-19** were plotted versus Hammett substituent parameters (**Figure 5.4**), a general trend was observed, wherein EW nitro substituted catalysts (**14-16**) have positive Hammett substituent parameters and lower branching densities than unsubstituted catalyst **13**. In contrast, catalysts bearing ED methoxy substituents (**17-19**) have negative Hammett parameters and higher branching densities than unsubstituted catalyst **13**. However, these empirical parameters were unable to capture the effects of three important factors in our study: electron donation or withdrawal via resonance versus induction, multiple substituents, and different locations of substituents in the molecule. Therefore, we sought another metric by which the electronic nature of each catalyst could be quickly measured, but that would also more accurately represent the often subtle variations in PE branching density obtained when using each catalyst.

Because placement and nature of EW and ED substituents is anticipated to alter the electronic nature of the catalyst, we hypothesized that electrochemical $E_{1/2}$ might provide a direct correlation to branching density. To this end, CV studies were conducted for catalysts **14-19** with dichloromethane as the solvent, $[nBu_4N][PF_6]$ (0.2 M) as the supporting electrolyte, and operating at a scan rate of 100 mV s⁻¹ (**Figure A.138- A.144, Table 5.1**). These $E_{1/2}$ values were then compared to unsubstituted catalyst **13**, which exhibited a $E_{1/2}$ at -0.90 V (vs. Fc/Fc⁺) (**Table 5.1**). When EW nitro substituents were included onto the ligand scaffold (**14-15**) the $E_{1/2}$ decreased to -0.64 and -0.61 V (vs. Fc/Fc⁺), respectively. Conversely, when ED methoxy substituents were appended onto the ligand scaffold (**17-19**) the $E_{1/2}$ remained similar to unsubstituted catalyst **13** or increased slightly to -0.94, -0.86, and -0.99 V (vs. Fc/Fc⁺), respectively. When measuring the $E_{1/2}$ of **16**, multiple, overlapping signals of varying intensity were observed making it difficult to determine a single, reliable $E_{1/2}$ value (**Figure A.141**) and was

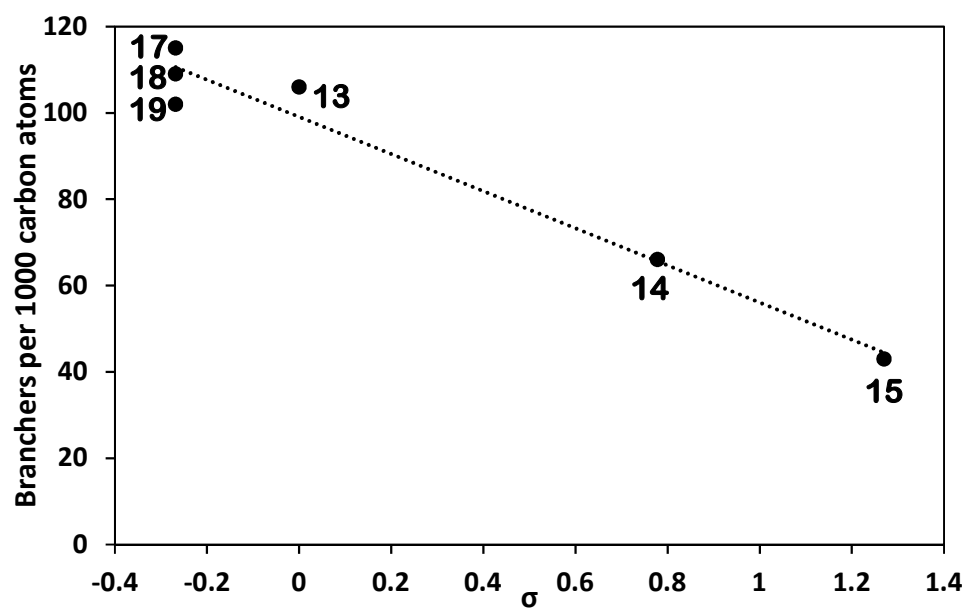


Figure 5.4 Plot of branches per 1000 carbon atoms vs. Hammett substituent parameters for catalyst 13-15, 17-19.

therefore not included in subsequent investigations.

Plotting PE branching density as a function of measured $E_{1/2}$ of catalysts **13-15** and **17-19** revealed a clear trend in which catalysts with more negative $E_{1/2}$ values produce more branches/1000 carbons (**17-19**) and catalysts with less negative $E_{1/2}$ produce fewer branches/1000 carbons (**14-15**), as compared to unsubstituted catalyst **13** (**Figure 5.5**). In addition to a qualitative trend, **Figure 5.5** shows that experimentally obtained PE branching density versus catalyst $E_{1/2}$ values can be represented by a linear function: $B = m(E_{1/2}) + c$, where B = branches/1000 carbons, m = slope, and c = intercept. The slope of the linear fit shows that an increase in $E_{1/2}$ of the catalyst by 0.1 V decreases the branching content of PE by about 18 branches/1000 carbons. This clear yet simple quantitative structure-branching relationship presents the opportunity to apply the linear function as a calibration curve to predict the branching density of PE produced with other Ni-based α -diimine catalysts, simply by experimentally measuring their $E_{1/2}$.

To better understand the mechanistic details underlying the observed modulation of PE branching as a function of incorporated EW and ED substituents, theoretical branching densities were calculated using density functional theory (DFT) as implemented within the Gaussian 16 software.²²⁹ The dispersion-corrected and range-separated hybrid exchange-correlation functional, WB97XD²³⁰, was used, which is designed to model systems with long-range charge transfer more accurately. Optimized geometries and their vibrational frequencies were calculated using the Ahlrichs def2svp basis set²³¹, and electronic energies of the relaxed geometries were calculated using the Ahlrichs def2tzvpp basis set²³¹ in a polarized continuum model of the toluene solvent.²³² All wavefunctions were checked for stability, and free energies were calculated at 298 K. The PE branching density was calculated from the free energy of isomerization of the square-planar catalytic intermediate (**I-3^{n-pr}**, **Scheme 5.2**) with a bound ethylene ligand and an *n*-propyl ligand to the corresponding complex with an *iso*-propyl ligand (**I-3^{i-pr}**, **Scheme 5.2**). This isomerization equilibrium was determined to dictate branching density, as was shown in our previous studies.¹⁹⁵ Further details, including the equation used to calculate the PE branching densities from DFT-computed free energies, are provided in Appendix A.6.

Scheme 5.2 Catalytic Reaction Pathway for Ethylene Polymerization Using a Ni-based α -Diimine Catalyst

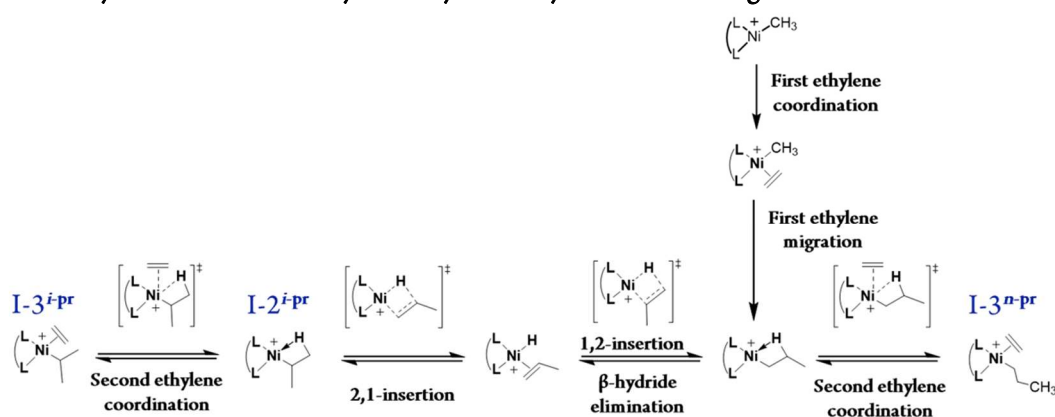


Figure 5.6 shows the theoretical PE branching densities produced by catalysts **13-15** and **17-19** as a function of experimentally determined $E_{1/2}$. These results support the trend observed experimentally (**Figure 5.5**) in which catalysts with more negative $E_{1/2}$ values (**13, 17-19**) are predicted to produce greater branching densities, whereas catalysts with less negative $E_{1/2}$ values (**14-15**) are predicted to produce lower branching densities. The

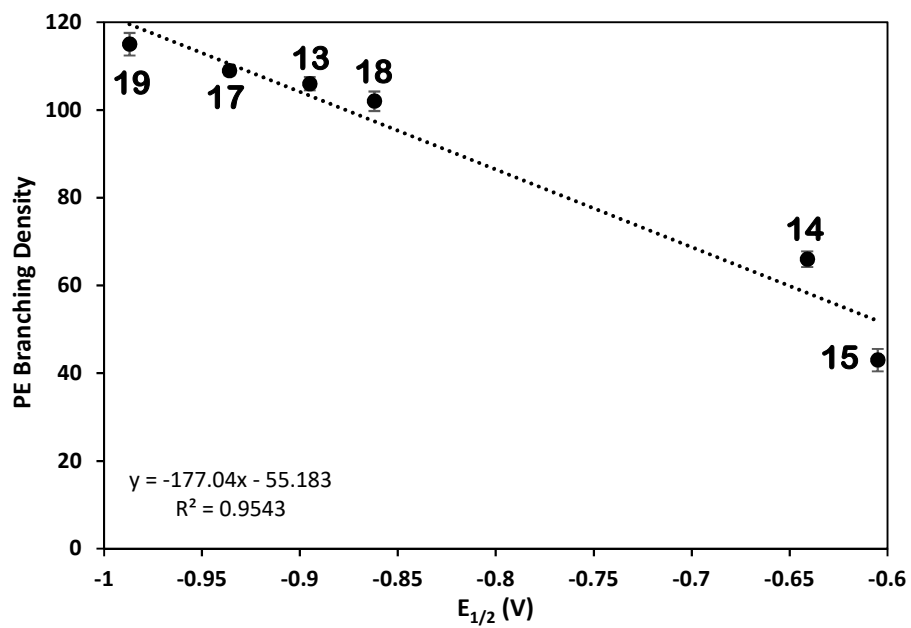


Figure 5.5 Plot of experimental PE branching density vs. experimental $E_{1/2}$ (V) for 13-15 and 17-19.

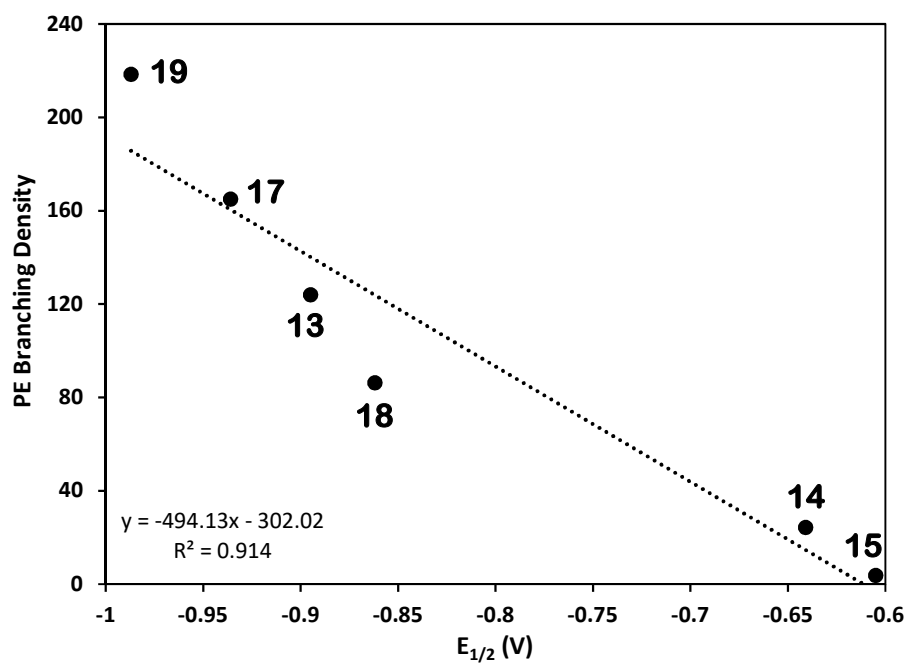


Figure 5.6 Plot of theoretical PE branching density vs. experimental $E_{1/2}$ (V) for 13-15 and 17-19.

theoretical PE branching density can also be fit to a linear function with an m value that differs from the experimental m value by a factor slightly less than 3. A structural analysis of the DFT results (**Appendix A.6.6**) reveals that EW substituents shift the isomerization equilibrium between **I-3^{pr}** and **I-3^{pr}** toward **I-3^{pr}** (favoring less branched PE) by strengthening the Ni-ethylene interaction in **I-3^{pr}** and concurrently weakening the β -agostic interaction between Ni and the *iso*-propyl ligand in **I-3^{pr}**. This weakening of the β -agostic interaction can be seen by the shortening of the C $_{\beta}$ -H $_{\beta}$ bond length (**Figure 5.7**, green circles), as well as the lengthening of the Ni-H $_{\beta}$ distance (**Figure 5.7**, blue circles) for catalysts **14** and **15**, compared to **13**. Conversely, ED substituents show the opposite effect by weakening the Ni-ethylene interaction in **I-3^{pr}** and strengthening the β -agostic interaction between Ni and the *iso*-propyl ligand in **I-3^{pr}**, thereby shifting the equilibrium toward **I-3^{pr}**, promoting β -hydride elimination, and favoring more branched PE. This strengthening of the β -agostic interaction can be seen by the shortening of the Ni-H $_{\beta}$ distance (**Figure 5.7**, blue circles) for catalysts **17** and **19**, compared to **13**.

Having established a correlation between PE branching and catalyst $E_{1/2}$, we sought to examine the predictive capabilities of this method. To do this, we synthesized five additional catalysts with expected $E_{1/2}$ values within the range of our calibration curve (catalysts **20-24**, **Figure 5.8**). As previously discussed, synthesis of nitroacenaphthoquinone yielded two isomers (**Figure 5.3**), but only one of which was used for the aforementioned studies. Having also isolated pure 4-nitroacenaphthoquinone, this synthon was used to access catalyst **20** that enabled us to simultaneously investigate the effect that EW nitro substituent placement on the acenaphthene backbone has on PE branching density. Catalysts bearing halide substituents (Br and Cl, catalysts **21-23**) were also chosen as they were expected to exhibit $E_{1/2}$ values between those seen for **14-15** and **13**, **17-19**; however, they would also enable us to apply our predictive curve to substituents that are inductively EW but may donate electron density via the ligands π -system. Lastly, a catalyst bearing methyl substituents (**24**) was chosen as it is expected to be slightly ED and fall within the $E_{1/2}$ range of catalysts **13** and **17-19**. Catalysts **20-24** were synthesized following similar synthetic routes as catalysts **14-19** (see **Appendix A.5**) and were all characterized using standard analytical techniques.

The $E_{1/2}$ of catalysts **20-24** were measured using CV under identical conditions as catalysts **13-19** (**Figure A.145-A.149**, **Table 5.2**). As expected, the reduction potential for catalyst **20** was similar to the other nitro substituted catalysts ($E_{1/2}$ = -0.69 V (vs. Fc/Fc⁺)), catalysts **21-23** were between those of the nitro substituted catalysts and the methoxy substituted catalysts ($E_{1/2}$ = -0.80, -0.78, and -0.79 V (vs. Fc/Fc⁺), respectively), and catalyst **24** was within the range of the methoxy substituted catalysts ($E_{1/2}$ = -0.87 V (vs. Fc/Fc⁺)). Using the measured $E_{1/2}$ values of catalysts **20-24**, the PE branching density was then predicted using the fitting function generated by the experimental calibration curve (**Figure 5.9**, triangles), prior to performing any polymerization trials. The predicted PE branching densities were 66, 87, 82, 85, and 100 branches/1000 carbons for catalysts **20-24**, respectively (**Table 5.2**).

The ethylene polymerization activity of catalysts **20-24** was then evaluated at 15 psi of ethylene using PMAO-IP as an activator (**Table 5.2**). The experimental branching density (**Figure 5.9**, circles) for catalysts **20** and **22** (64 ($\pm$ 2) and 82 ($\pm$ 1) branches/1000 carbons, respectively) were in very close agreement with predicted values. Catalysts **21** and **23** produced PE with 103 ($\pm$ 4) and 79 ($\pm$ 1) branches/1000 carbons, respectively, and were also within reasonable agreement with the predicted values. However, the experimental branching density of **24** was significantly lower than expected at only 71 ($\pm$ 3) branches/1000 carbons (versus predicted value of 100 branches/1000 carbons). This difference is believed to be due to methyl substituent's inability to efficiently donate or withdraw electron density through the ligands π -system, whereas all other catalysts tested (**14-23**, bearing NO₂,

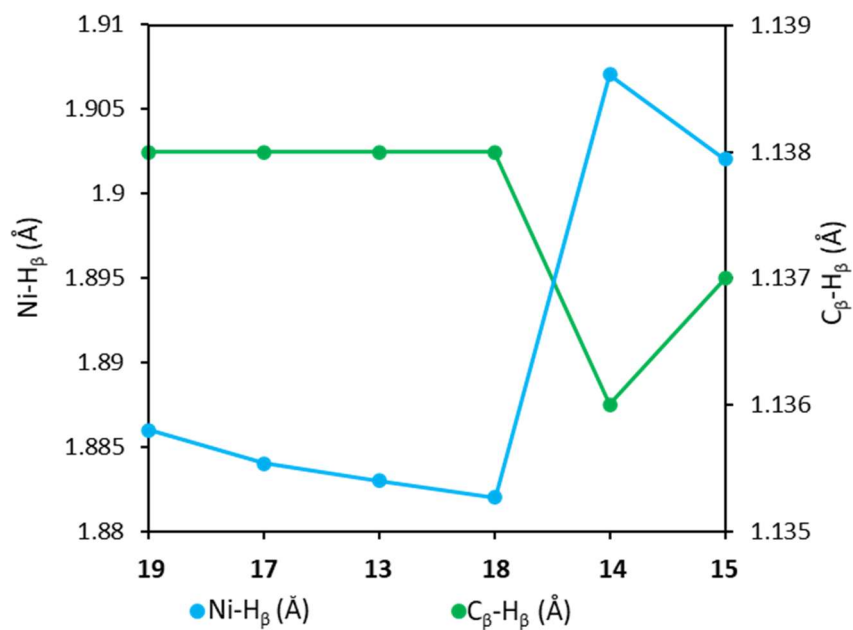


Figure 5.7 Plot of C β -H β bond lengths (Å, green circles) and Ni-H β distance (Å, blue circles) for catalysts 13-15 and 17-19.

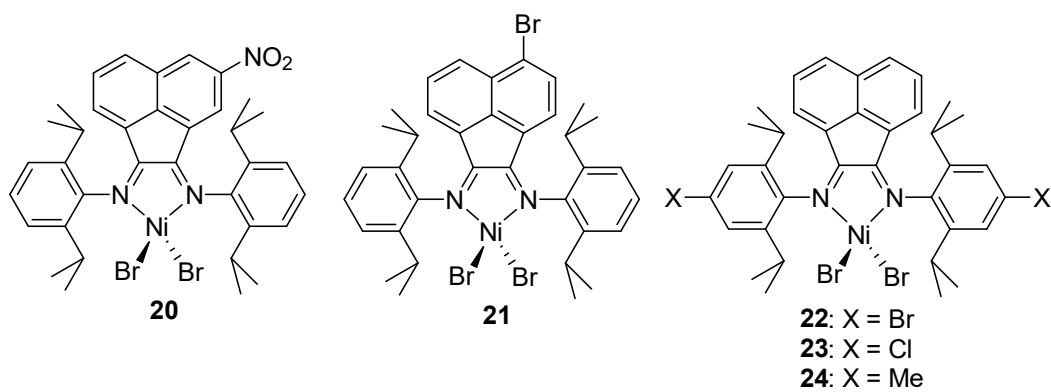


Figure 5.8 Structures of catalysts 20-24.

Table 5.2 Polymerization of Ethylene Using Catalysts **20-24**.^a

Catalyst	Yield (g)	M_n^b (kg/mol)	$\bar{D}^b$	$E_{1/2}$ (V)	B (pred.)	B (exp.) ^c
20	2.6	184	2.29	-0.69	66	64 (± 2)
21	1.1	99	1.67	-0.80	87	103 (± 4)
22	1.3	111	2.23	-0.78	82	82 (± 1)
23	1.6	130	1.97	-0.79	85	79 (± 1)
24	1.0	205	2.27	-0.87	100	71 (± 3)

^aPolymerization Conditions: 15 psi ethylene, 0.01 mmol catalyst, 0.92 mmol PMAO-IP, 148 mL toluene, 2 mL DCM, 30 min. ^bDetermined using triple detection gel permeation chromatography at 140 °C in 1,2,4-trichlorobenzene. ^cBranches/1000 carbons, determined by ¹H NMR at 100 °C in C₂D₂Cl₄,²²⁷ values are reported as averages over multiple polymerization trials and error is reported as one standard deviation.

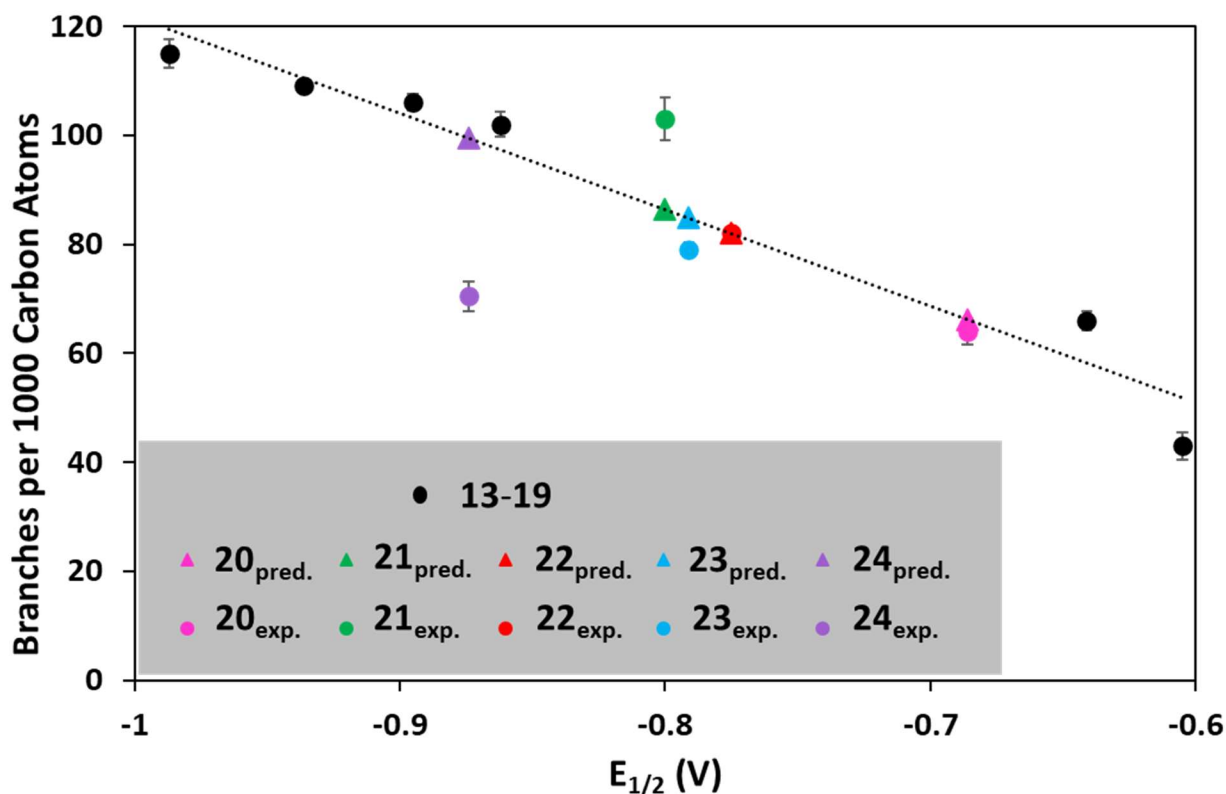


Figure 5.9 Experimental calibration curve with predicted (triangles) and experimental (circles) branching density (branches/1000 carbons) for **20** (pink), **21** (green), **22** (red), **23** (blue), and **24** (purple). Predicted values determined using the fit generated with the experimental calibration curve. Note: the predicted and experimental markers for **20** and **22** coalesce.

OMe, Br, and Cl substituents) may do so. We hypothesize that a primarily σ -donating substituent (such as methyl) will decrease the electrophilicity of Ni by donating electron density to the empty Ni d-orbital that overlaps with the filled C_{β} - H_{β} σ orbital of ethylene. This could result in the weakening of the β -agostic interaction and decrease PE branching density, as was observed experimentally. When the theoretical PE branching density for catalyst **24** was determined computationally a decrease in branching density, as compared to catalysts **13**, was calculated (18 vs. 124 branches/1000 carbons, respectively) supporting our experimental observations.

5.3 Conclusion

In summary, we have systematically examined how placement of EW and ED substituents on either the acenaphthene-derived backbone, *N*-aryl moieties, or both impact the degree of PE branching obtained when using Ni-based α -diimine olefin polymerization catalysts. Our results demonstrate that catalysts bearing EW nitro substituents (**14-16**) produce PE with decreased branching density as compared to unsubstituted catalyst **13**. We hypothesize that this difference in PE branching density arises from the π -withdrawing nature of nitro substituents, which withdraws electron-density from the filled d-orbital at the Ni-center, decreasing π -backbonding with the empty C_{β} - H_{β} σ^*_{2p} of ethylene, weakening the β -agostic interaction, decreasing the likelihood of β -hydride elimination, and decreasing PE branching density. In contrast, catalysts bearing ED methoxy substituents (**17-19**) produced PE with little to no change in PE branching density as compared to unsubstituted **13** under identical polymerization conditions.

We demonstrated that as the electronic nature of Ni-based α -diimine catalysts are varied as a function of EW and ED substituent identity, number (1 vs. 2 vs. 3), and placement (backbone vs. *N*-aryl moiety), so too is the reduction potential ($E_{1/2}$) of those catalysts. Plots of PE branching density as a function of catalysts' $E_{1/2}$ values yield a linear trend in which catalysts bearing more negative $E_{1/2}$ values produce PE with a higher branching density (**13**, **17-19**) and catalysts with more positive $E_{1/2}$ values produce PE with a lower branching density (**14-15**). This linear trend was then leveraged to generate a calibration curve.

DFT was used to better understand the mechanistic details behind the observed modulation of PE branching density as a function of EW and ED group incorporation. These results support our experimentally observed trend in which incorporation of EW substituents decreases PE branching density due to a shift in the isomerization equilibrium between **I-3^{ap}** and **I-3^{ip}** toward **I-3^{ap}**. This shift in equilibrium is due to strengthening of the Ni-ethylene interaction in **I-3^{ap}** and concurrent weakening of the β -agostic interaction between Ni and the *iso*-propyl ligand in **I-3^{ip}**, which can be seen computationally by the shortening of the C_{β} - H_{β} bond length, as well as lengthening of the Ni- H_{β} distance. Conversely, inclusion of ED substituents shows the opposite effect via the weakening of the Ni-ethylene interaction in **I-3^{ap}** and strengthening of the β -agostic interaction between Ni and the *iso*-propyl ligand in **I-3^{ip}** (shortening of the Ni- H_{β} distance), thereby shifting the equilibrium toward **I-3^{ip}**.

Lastly, we examined the predictive powers of the observed relationship between catalyst $E_{1/2}$ and PE branching density through the synthesis of five new Ni-based α -diimine catalysts (**20-24**). The experimental PE branching densities of catalysts **20-23** were found to be within good agreement of the predicted values; however, the experimentally measured PE branching density when using catalyst **24** was much lower than predicted. This is hypothesized to be due to methyl substituent's inability to efficiently donate or withdraw electron density through the ligands π -system, which differs from the other catalysts studied (**14-23**). We anticipate that the predictive

method established herein may be used to strategically design future Ni-based α -diimine-based catalysts that produce targeted PE branching densities, without the need for exhaustive polymerization studies.

Chapter 6 - Summary and Future Work

6.1 Summary

Through the work presented herein, three distinct catalyst studies were conducted to study how a variety of ligand scaffold modifications affect the catalytic activity, selectivity, and/or polymer topology during the polymerization of either cyclic esters, such as L-LA or CL, or ethylene. The initial portion of this dissertation (Chapters 1-3) laid the foundation for the development of redox-active ROP catalysts and detailed the contributions that our group has made to this area of study. First, we examined how the number of redox-active moieties, ligand denticity, and active metal center identity affected the catalytic activity and redox-switchability via the comparison of a symmetric, tetradentate [ONNO] Ti-based catalyst bearing two redox-active moieties (**1**) to an asymmetric, tridentate [ONN] Ti- or Zr-based catalyst bearing only a single redox-active moiety (**10_{Ti}** and **10_{Zr}**, respectively). When tested for the polymerization of L-LA it was found that both **1** and **10_{Ti}** were active in their native states and dramatically less active in their oxidized states but with **10_{Ti}** polymerizing L-LA approximately 3× slower than **1**. Additionally, the on/off ratios for catalysts **1** and **10_{Ti}** were found to be within error of one another (57 (± 14) and 44 (± 23), respectively). These results suggest that the number of redox-active moieties may not play a crucial role in these catalysts' ability to differentiate catalytic activity as a function of ligand-based oxidation state (redox-switchability), but that the number of redox-active moieties and/or ligand denticity may indeed impact the overall rate of polymerization. Conversely, **10_{Zr}** exhibited a rate of polymerization ~5× faster than that of **10_{Ti}** and the on/off ratios for the polymerization of L-LA were roughly double that of **10_{Ti}** (82 (± 25)), suggesting that the identity of the active metal center may drastically influence catalytic stability, activity, and overall redox-switchability.

Next, we examined how ligand connectivity and conjugation and metal center identity affect the catalytic activity, selectivity, and redox-switchability of these redox-active ROP catalysts. These factors were investigated through the comparison of the polymerization behavior of two [ONNO] salen-type catalysts with group IV metal centers bearing two ferrocenyl moieties (**1_{Ti}** and **1_{Zr}**) to the behavior of two [ONNO]salan-type catalysts with group IV metal centers bearing two ferrocenyl moieties (**12_{Ti}** and **12_{Zr}**) for the polymerization of L-LA and CL. Through comparison of these catalysts, it was shown that salen-type catalysts **1_{Ti}** and **1_{Zr}** and salan-type catalysts **12_{Ti}** and **12_{Zr}** are all active for the ROP of L-LA and CL in their native states and are significantly less active in their oxidized states. Additionally, in all cases the Zr-based catalysts (**1_{Zr}** and **12_{Zr}**) exhibited higher activities than their Ti-based analogues (**1_{Ti}** and **12_{Ti}**).

For the polymerization of L-LA, it was seen that both salan-type catalysts were more active than their salen-type analogues with catalyst **12_{Ti}** polymerizing L-LA 1.2× faster than **1_{Ti}** and catalyst **12_{Zr}** polymerizing L-LA 3.3× faster than **1_{Zr}**. Catalysts **1_{Ti}** and **12_{Ti}** were also seen to have drastically different switching performances, yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of 130 (± 27) and 31 ± (2), respectively. In contrast, catalysts **1_{Zr}** and **12_{Zr}** exhibited similar differentiation in polymerization activity between the native and oxidized states, yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of 1290 (± 645) and approaching infinity, respectively. Whereas for the polymerization of CL, catalyst **12_{Ti}** polymerized CL 12.3× faster than **1_{Ti}** and catalyst **1_{Zr}** polymerized CL 1.7× faster than **12_{Zr}**. Moreover, both salan-type catalysts exhibited a greater differentiation in polymerization activity between the native and oxidized states than salen-type catalysts with **12_{Ti}** and **1_{Ti}** yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of 49 ± (16) and 36 (± 11), respectively, while **12_{Zr}** and **1_{Zr}** yielding $k_{obs}^{native}/k_{obs}^{oxidized}$ ratios of 44 (± 7) and 23 (± 3), respectively. We hypothesize that as the architecture of the ligand is varied (salen vs. salan), the electronic communication through the ligand scaffold, as

well as the geometric configuration of the catalyst, may be altered leading to the changes in catalytic activity, selectivity, and redox-switchability observed.

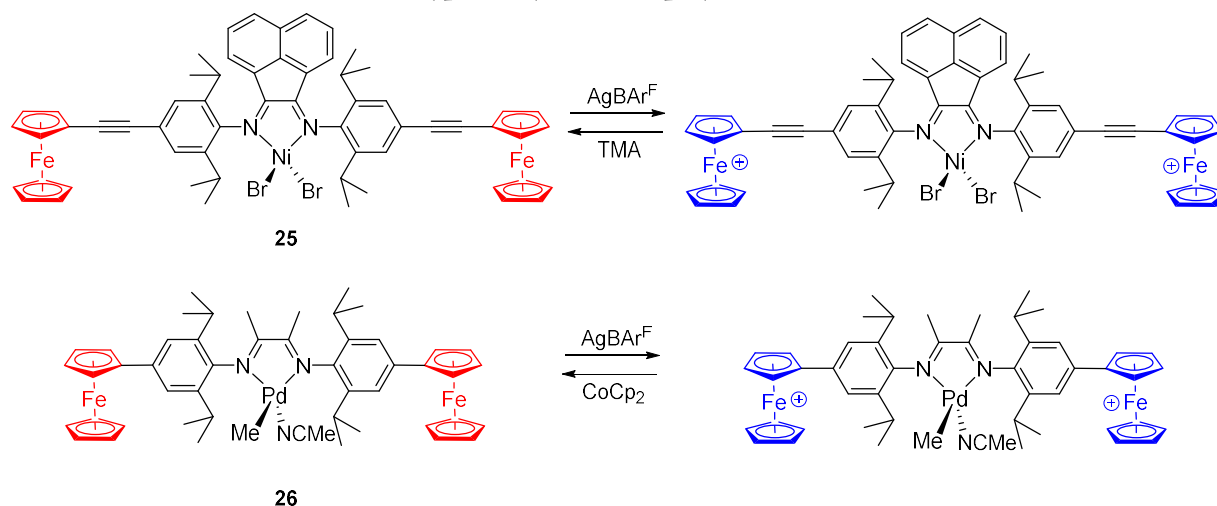
However, the mechanistic rationale for the changes in catalytic activity, selectivity, and redox-switchability with modification to ligand denticity, number of redox-active moieties, ligand connectivity, conjugation of the ligand scaffold, and active metal center identity are not fully understood at this time. Therefore, computational examination of the key transition states and intermediates involved in the initiation and propagation for the ROP of L-LA and CL using each catalyst could provide valuable insight and a deeper understanding of the experimentally observed changes in catalytic behavior. These investigations may be the subject of future investigations in the Long group.

In the subsequent portion of this dissertation (Chapters 4 and 5), we examined the design of late transition metal-based α -diimine catalysts for the polymerization of ethylene and how modification to the electronic nature of the ligand scaffold affects the topology of the resulting PE produced. This resulted in the synthesis of 11 novel Ni-based catalysts (**14-24**) bearing EW or ED substituents on either the acenaphthene derived backbone, the *N*-aryl moieties, or on both the acenaphthene derived backbone and the *N*-aryl moieties. The PE branching density of **14-19** was compared to that of unsubstituted catalyst **13** and it was found that inclusion of EW nitro substituent(s) resulted in a decrease in PE branching density but inclusion of ED methoxy substituent(s) resulted in no change or a slight increase in the PE branching density. Furthermore, it was found that when the PE branching density was plotted against the catalysts' reduction potential ($E_{1/2}$) a linear trend emerged which could be used to predict the branching density of other novel Ni-based acenaphthene derived α -diimine catalysts with EW (halide or nitro) or ED (methyl) substituents (**20-24**). The results of all three of these studies offer fundamental insight into the design of polymerization catalysts whose catalytic activity, selectivity, and/or resulting polymer topology can be modulated to access a variety of tailorable polymeric materials.

6.2 Future Work

Moving forward, our group will continue to design and study redox-active polymerization catalysts with a particular interest targeting redox-active α -olefin polymerization catalysts. In 2017 Long and coworkers investigated a new Ni-based, ferrocene containing α -diimine catalyst with an acenaphthene derived backbone (**25**, **Scheme 6.1**) to determine how oxidation of an α -diimine ligand scaffold affected ethylene polymerization activity and PE topology.¹⁹⁶ By comparing the PE branching density obtained with their novel catalyst in the native state to that of the previously reported non-ferrocene containing Ni-based α -diimine catalyst with an acenaphthene derived backbone a decrease from 114 branches per 1000 carbon atoms to 40 branches per 1000 carbon atoms was observed which was attributed to the ferrocenyl moieties donating electron density to the metal center resulting in a decrease in chain-walking events versus propagation events.^{196, 197} Therefore it was hypothesized that upon oxidation of the ferrocenyl moieties the branching density may increase due to the ferrocenyl moieties withdrawing electron density away from the active metal center resulting in an increase in chain-walking events versus propagation events. Unfortunately, however, upon oxidation of the ferrocenyl moieties with AgBAR^F, no difference in polymerization activity or polymer topology was observed as compared to the native state of **25**. It was hypothesized that the trimethylaluminum (TMA) present in the MAO cocatalyst acts as a reductant, negating the added oxidant and resulting in no overall change to the electron density of the catalyst system.

Scheme 6.1 Redox-active α -diimine-type catalysts for the polymerization of α -olefins



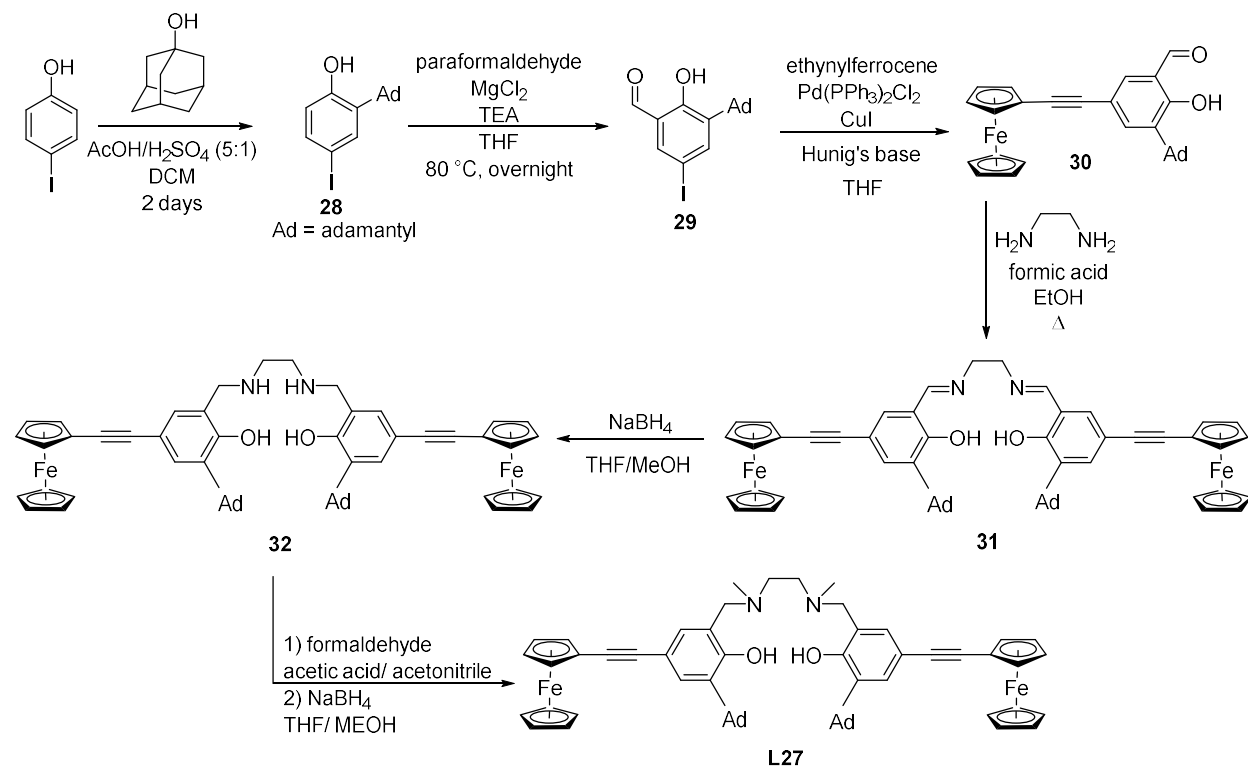
Chen and colleagues expanded this class of redox-active olefin polymerization catalysts to include a Pd-based α -diimine catalysts with ferrocenyl moieties (**26**, Scheme 6.1) that can be activated with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate (NaBAR^{F}) instead of MAO allowing the researchers to examine the effects of oxidation of the ferrocenyl moieties on polymerization activity and polymer topology.²²⁰ When tested for the polymerization of ethylene, the native, partially oxidized (1 equivalent AgBAR^{F}), and fully oxidized (2 equivalents AgBAR^{F}) forms of **26** were all highly active but produced PE with different branching topologies. Upon increased oxidation an increase in the number of branch-on-branch structures was seen leading to a more hyperbranched like PE. Furthermore, when examined for the polymerization of 1-hexene, the activity of **26** was seen to change with an increase in oxidation leading to decrease in polymerization activity ultimately leading to an inactive catalyst. This decrease in polymerization activity was attributed to an increase in electrophilicity of the metal center resulting in an increase in chain transfer as compared to chain propagation.

Therefore, in order to expand the field of redox-active α -olefin polymerization catalysts we will shift our focus to other classes of catalysts that do not require the use of MAO or TMA as a cocatalyst. One very promising catalyst class is the salen-type ligands with group IV active metal centers. The non-redox-active variants of these catalysts have been extensively explored by Kol and coworkers for the polymerization of α -olefins and have been shown to be moderately to highly active for the polymerization of ethylene and 1-hexene.²³³⁻²³⁹ Through this work Kol and coworkers have shown that inclusion of sterically bulky substituents ortho to the phenol moieties can be used to increase the catalyst's polymerization activity. Therefore, we propose the development of a salen-type catalyst with adamantyl substituents ortho to the phenol moieties bearing two redox-active ferrocenyl moieties distal to the active metal center (**27**, Figure 6.1) in order to study how modulation of the electron density at or around the metal center with oscillation of the ferrocenyl moieties oxidation state affects catalytic activity and resulting polymer topology for the (co)polymerization of ethylene and 1-hexene.

As preliminary work, **L27** has been synthesized as described in Scheme 6.2. First, commercially available 4-iodophenol was adamantylated with 1-adamantanol with acetic acid and sulfuric acid in DCM to obtain **28**.^{240, 241} Next, **28** was formylated via reaction with paraformaldehyde, MgCl_2 , and triethylamine in THF at 80 °C overnight to yield **29**.²⁴² Compound **29** was then coupled with ethynylferrocene¹⁶² via Sonogashira coupling using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, and Hunig's base in THF to form **30**. Diimine **31** was then reduced with NaBH_4 in 50:50 THF:

MeOH (**32**), followed by methylation with formaldehyde in acetic acid and acetonitrile, then reduction with NaBH_4 in 50:50 THF: MeOH to yield **L27**.

Scheme 6.2 Synthesis of [ONNO]-type ligand L27



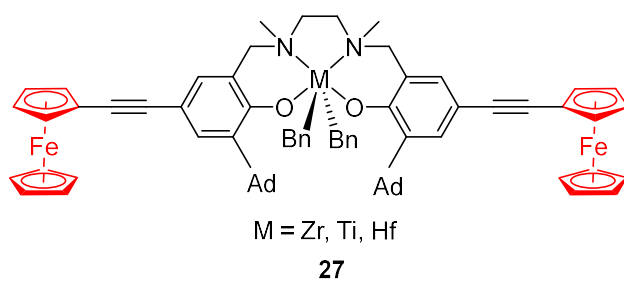


Figure 6.1 Proposed structure of redox-active salen-type catalyst with a group IV active metal center.

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Appendices

Appendix A - Experimental and Supporting Information

A.1 Experimental – Chapter 2

A.1.1 General Methods and Materials.

Toluene, ether, hexanes, and pentanes were purified using a two-column purification system and degassed via freeze-pump-thaw (x3). Benzene was dried over activated molecular sieves and degassed prior to use. All NMR solvents were purchased from Cambridge Isotope Laboratories, and C_6D_6 and $CDCl_3$ were dried over activated molecular sieves and degassed prior to use. 1H and ^{13}C NMR spectra were recorded on a Varian 300, Bruker 400, or Varian 400 MHz spectrometer. Chemical shifts are reported with respect to solvent residual peaks, 7.26 ppm ($CDCl_3$), 7.16 ppm (C_6D_6) or 2.05 (acetone- d_6). L-Lactide was purchased from Fisher Scientific and recrystallized three times from toluene prior to use. 2,4-di-tert-butyl-6-((2-dimethylamino)ethylimino)methyl)-phenol (**L11**),¹⁵⁴ ethynyl-ferrocene,¹⁶² 3-tert-butyl-5-iodosalicylaldehyde,¹⁶³ 3-tert-butyl-5-ethynylferrocene-salicylaldehyde,⁹⁰ and **1**⁹⁰ were synthesized following previously reported procedures. Silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was synthesized by a modified literature procedure.²⁴³⁻²⁴⁵ All other reagents were purchased from commercial vendors and used without further purification. Elemental microanalyses were carried out by Atlantic Microlab, Inc. (Norcross, GA). X-ray diffraction measurements were performed on a single crystal Bruker Kappa DUO diffractometer. Cyclic voltammetry measurements were performed on a CH Instruments potentiostat using 0.01 mmol of the compound to be analyzed in 5 mL DCM solution (0.002 M) with supporting electrolyte 0.2 M (nBu)₄NPF₆, using Ag/AgCl as the reference electrode, a gold working electrode, and a tungsten counter electrode at a scanning rate of 100 mV·s⁻¹. All potentials are referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. Molecular weights (M_n) and dispersity ($\bar{D}$) of the polymers were determined using a Malvern Omisec system using triple detection and three Viscotek styrene divinylbenzene copolymer columns (in series T3000, T4000, and T5000) at a flow rate of 1 mL/min and thermostatted to 30 °C with THF as the eluent.

A.1.2 Synthesis of $C_{27}H_{32}N_2OFe$ (**L10**)

To a 50:50 mixture of ethanol: THF (8mL), was added 3-tert-butyl-5-ethynylferrocene-salicylaldehyde (0.5 g, 1.29 mmol), N,N-dimethylethylenediamine (0.17 mL, 1.55 mmol), and ~10 drops of formic acid. The resulting mixture was stirred at 80 °C overnight. All volatiles were then removed under reduced pressure and product **L10** was obtained as an orange solid after recrystallization from hexanes followed by a silica plug with a hexane/DCM eluent. Yield: 52% (0.31 g, 0.67 mmol). 1H NMR (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 1.44 (s, 9H), 2.31 (s, 6H), 2.66 (t, 2H), 3.71 (t, 2H), 4.21 (t, 2H), 4.25 (s, 5H), 4.48 (t, 2H), 7.28 (d, 1H), 7.42 (d, 1H), 8.32 (s, 1H). ^{13}C NMR (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 29.3, 35.0, 45.86, 45.89, 57.4, 59.9, 65.9, 68.7, 70.0, 71.3, 85.8, 85.9, 112.9, 118.5, 132.6, 132.9, 138.0, 161.0, 165.8. HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{27}H_{32}N_2OFe$, 456.19; found, 456.84.

A.1.3 Synthesis of $(C_{27}H_{31}N_2OFe)Ti(O^iPr)_2$ (**10_{Ti}**)

Under an inert atmosphere, $Ti(O^iPr)_4$ (0.16 mL, 0.55 mmol) was added dropwise to a toluene solution (5 mL) of **L10** (0.25 g, 0.55 mmol) and stirred overnight. The volatiles were removed under reduced pressure and the resulting orange solid was recrystallized from hexanes to yield complex **10_{Ti}**. Yield: 44% (0.16 g, 0.24 mmol). Crystals suitable for X-ray crystallography were obtained by recrystallization from hexanes upon cooling to -20 °C. 1H NMR (300 MHz, 25 °C, C_6D_6), δ , ppm: 1.20 (d, 18H), 1.62 (s, 9H), 2.13 (t, 2H), 2.44 (s, 6H), 2.94 (t, 2H), 3.97 (t, 2H), 4.15 (s, 5H), 4.56 (t, 2H), 4.71 (br, 3H), 7.38 (d, 2H), 7.87 (d, 1H). ^{13}C NMR (300 MHz, 25 °C,

C₆D₆), δ , ppm: 26.8, 29.7, 35.5, 49.8, 56.0, 60.0, 67.3, 68.8, 70.2, 71.5, 74.0, 86.1, 87.5, 111.3, 122.3, 135.0, 135.9, 139.4, 161.5, 164.8. Elemental analysis for C₃₆H₅₂N₂O₄FeTi (680.53 g/mol): Calc'd: 63.54% C, 7.70% H, 4.12% N; Found: 62.41% C, 7.25% H, 4.00% N. We attribute the discrepancy in the elemental analysis to the presence of silicon grease and although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

A.1.4 Synthesis of (C₂₇H₃₁N₂OFe)Zr(OⁱBu)₃ (10_{Zr})

Under an inert atmosphere, Zr(OⁱBu)₄ (0.21 mL, 0.55 mmol) was added dropwise to a toluene solution (5 mL) of **L10** (0.25 g, 0.55 mmol) and stirred overnight. The volatiles were removed under reduced pressure and the resulting orange solid was recrystallized from hexanes to yield complex **10_{Zr}**. Yield: 48% (0.20 g, 0.26 mmol). Crystals suitable for X-ray crystallography were obtained by recrystallization from hexanes upon cooling to -20 °C. ¹H NMR (300 MHz, 25 °C, C₆D₆), δ , ppm: 1.2 (s, 18H), 1.54 (s, 9H), 1.61 (s, 9H), 2.24 (t, 2H), 2.38 (s, 6H), 2.98 (t, 2H), 3.97 (t, 2H), 4.14 (s, 5H), 4.56 (t, 2H), 7.33 (s, 1H), 7.38 (d, 1H), 7.88 (d, 1H). ¹³C NMR (300 MHz, 25 °C, C₆D₆), δ , ppm: 30.1, 33.4, 35.5, 49.2, 55.7, 59.9, 67.3, 68.8, 70.2, 71.5, 73.0, 85.9, 87.6, 111.1, 123.0, 135.4, 136.7, 140.1, 163.7, 164.2. Elemental analysis for C₃₉H₅₈N₂O₄FeZr (765.97 g/mol): Calc'd: 61.16% C, 7.63% H, 3.66% N; Found: 61.29% C, 7.54% H, 3.39% N.

A.1.5 Synthesis of (C₁₉H₃₁N₂O)Ti(OⁱPr)₃ (11_{Ti})

Under an inert atmosphere, Ti(OⁱPr)₄ (0.24 mL, 0.82 mmol) was added dropwise to a toluene solution (10 mL) of **L11** (0.25 g, 0.82 mmol) and stirred overnight. The volatiles were removed under reduced pressure and the resulting solid was recrystallized from pentanes at -20 °C to yield **11_{Ti}** as a yellow solid. Yield: 30.8% (0.13 g, 0.25 mmol). Crystals suitable for X-ray crystallography were obtained via recrystallization from pentanes at -20 °C. ¹H NMR (300 MHz, 25 °C, C₆D₆), δ , ppm: 1.23 (d, 18H), 1.34 (s, 9H), 1.77 (s, 9H), 2.28 (t, 2H), 2.47 (s, 6H), 3.20 (t, 2H), 4.80 (m, 3H), 7.06 (d, 1H), 7.60 (s, 1H), 7.70 (d, 1H). ¹³C NMR (300 MHz, 25 °C, C₆D₆), δ , ppm: 26.9, 30.1, 31.7, 34.1, 35.8, 49.5, 56.3, 60.1, 74.2, 96.6, 121.6, 128.1, 129.2, 138.0, 162.5, 162.8. Elemental analysis for C₂₈H₅₂N₂O₄Ti (528.60 g/mol): Calc'd: 63.62% C, 9.92% H, 5.30% N; Found: 62.20% C, 9.80% H, 5.53% N. We attribute the discrepancy in the elemental analysis to the presence of silicon grease and although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

A.1.6 Synthesis of (C₁₉H₃₁N₂O)Zr(OⁱBu)₃ (11_{Zr})

Under an inert atmosphere Zr(OⁱBu)₄ (0.32 mL, 0.82 mmol) was added dropwise to a toluene solution (10 mL) of **L11** (0.25 g, 0.82 mmol) and stirred overnight. The volatiles were removed under reduced pressure and the resulting solid was recrystallized from pentanes at -20 °C to yield complex **11_{Zr}** as a white solid. Yield: 52.8% (0.27 g, 0.43 mmol). Crystals suitable for X-ray crystallography were obtained via recrystallization from pentanes at -20 °C. ¹H NMR (300 MHz, 25 °C, C₆D₆), δ , ppm: 1.22 (br, 18H), 1.32 (s, 9H), 1.56 (br, 9H), 1.77 (s, 9H), 2.34 (t, 2H), 2.43 (s, 6H), 3.18 (t, 2H), 7.08 (d, 1H), 7.54 (s, 1H), 7.71 (d, 1H). ¹³C NMR (300 MHz, 25 °C, C₆D₆), δ , ppm: 30.4, 31.7, 33.5, 34.1, 35.8, 49.3, 56.0, 60.1, 122.2, 128.9, 129.6, 137.3, 138.8, 162.0, 164.8. Elemental analysis for C₃₂H₅₈N₂O₄Zr (614.04 g/mol): Calc'd: 60.64% C, 9.52% H, 4.56% N; Found: 60.81% C, 9.80% H, 4.63% N.

A.1.7 Synthesis of Silver Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (AgBAR^F)

Silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (AgBAR^F) was prepared via a modified literature procedure.²⁴³⁻²⁴⁵ Mg turnings (0.654 g, 26.9 mmol) were added to a flame dried three-necked round bottom flask equipped with a reflux condenser, addition funnel, and septum. The reaction flask was evacuated and back-filled with N₂ (×3) and the Mg turnings were stirred for 2 hours under N₂. AgBF₄ (0.798 g, 4.1 mmol) was added under positive N₂ pressure followed by the addition of Et₂O (100 mL) via syringe. 1,2-dibromoethane (0.315 mL, 3.65 mmol) was then added dropwise via syringe and the flask was briefly heated with a heat gun until the solution became cloudy. Once refluxing stopped, Et₂O (34 mL) and 3,5-bis(trifluoromethyl)bromobenzene (4 mL, 23.2 mmol) were added to the addition funnel via syringe followed by dropwise addition over ~30 min. After complete addition, the reaction mixture was refluxed for 30 min followed by stirring at room temperature for 60 h. The reaction mixture was then added to a solution of Na₂CO₃ (10.6 g) in water (140 mL), stirred briefly, and filtered. The ether layer was separated, and the aqueous layer was extracted with ether (×3). The organic layers were combined, and the solvent was removed under vacuum. The crude solid was allowed to partially hydrate via exposure to air for 24 h. The solid was washed with minimal cold DCM to yield AgBAR^F as an off-white powder that was dried under vacuum at 100 °C over P₂O₅ for 18-24 h. Yield: 40% (1.58 g, 1.62 mmol). ¹H NMR (300 MHz, 25 °C, acetone-*d*₆), δ, ppm: 7.67 (s, 4H), 7.79 (s, 8H).

A.1.8 General NMR Scale Polymerization Procedure

In a glove box, L-lactide (0.7 mmol), catalyst (0.007 mmol), trimethoxybenzene (internal standard) (0.035 mmol), and solvent (0.7 mL) were added to a J. Young NMR tube equipped with a Teflon valve. The NMR tube was removed from the glove box, and the polymerization was monitored by ¹H NMR spectroscopy by placing the sample in a Bruker Avance 400 MHz NMR or Varian 400 MHz NMR operating at 90 °C. The commands “multizg” or the array “pad”, respectively, were used to collect data every 10 min and the data was processed using XWinNMR3.6 or VnmrJ 4.2, respectively. Conversion of L-lactide was monitored by comparing the relative intensities of the monomer’s methine peak to the methine peak of the polymer and referenced to the internal standard.

A.1.9 NMR Scale Polymerization using Oxidized Catalyst 1

In a glove box, catalyst 1 (0.007 mmol) was dissolved in C₆D₆ (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve that contained AgOTf (0.014 mmol). The tube was shaken to mix and heated at 90 °C for 30 min. After cooling to room temperature, L-lactide (0.7 mmol) and trimethoxybenzene (internal standard) (0.035 mmol) were added to the NMR tube, sealed, and removed from the glove box. The reaction mixture was heated to 90 °C and the polymerization was monitored by ¹H NMR spectroscopy using a Varian 400 MHz NMR. The array “pad” was used to collect data every 10 min and the data was processed with VnmrJ 4.2. Conversion of L-lactide was monitored by comparing the monomer’s methine peak to the methine peak of the polymer and referenced to the internal standard.

A.1.10 NMR Scale Polymerization using Oxidized Catalysts 10_{Ti} and 10_{Zr}

In a glove box, L-lactide (0.7 mmol) and either catalyst 10_{Ti} or 10_{Zr} (0.007 mmol) were added to a vial and dissolved in either C₆D₆ or CDCl₃ (0.7 mL). AgBAR^F (0.007 mmol) was added to the vial, shaken to mix, and then

filtered into a J. Young NMR tube containing trimethoxybenzene as an internal standard (0.035 mmol). The NMR tube was sealed, removed from the glove box, and the polymerization was monitored by ^1H NMR spectroscopy by placing the sample in a Bruker Avance 400 MHz NMR at 90 °C. The command “multizg” was used to collect data every 10 min. Conversion of L-lactide was monitored by comparing the monomer’s methine peak to the methine peak of the polymer and referenced to the internal standard.

A.1.11 NMR Scale Polymerization using Reduced Catalyst 1

In a glove box, catalyst **1** (0.007 mmol) was dissolved in C_6D_6 (0.7 mL) and the solution was added to a J. Young NMR tube equipped with a Teflon valve. AgOTf (0.014 mmol) was added to the NMR tube, then sealed and shaken to mix. The reaction mixture was heated to 90 °C for 30 min. After cooling to room temperature, CoCp_2 (0.014 mmol), L-lactide (0.7 mmol) and trimethoxybenzene (internal standard) (0.035 mmol) were added to the J. Young NMR tube. The NMR tube was sealed and removed from the glove box. The polymerization mixture was heated to 90 °C and monitored by ^1H NMR spectroscopy using a Varian 400 MHz NMR. The array “pad” was used to collect data every 10 min and the data was processed with VnmrJ 4.2. Conversion of L-lactide was monitored by comparing the monomer’s methine peak to the methine peak of the polymer and referenced to the internal standard.

A.1.12 NMR Scale Polymerization using Reduced Catalysts **10_{Ti}** and **10_{Zr}**

In a glove box, L-lactide (0.7 mmol) and either catalyst **10_{Ti}** or **10_{Zr}** (0.007 mmol) were added to a vial and dissolved in either C_6D_6 or CDCl_3 (0.7 mL). AgBAR^{F} (0.007 mmol) was added to the vial, shaken to mix, and then filtered into a J. Young NMR tube. Next, CoCp_2 (0.007 mmol) and trimethoxybenzene (internal standard) (0.035 mmol) were added to the NMR tube, which was sealed and removed from the glove box. The polymerization mixture was heated to 90 °C and monitored by ^1H NMR spectroscopy using a Bruker Avance 400 MHz NMR at 90 °C. The command “multizg” was used to collect data every 10 min and the data was processed with XWinNMR3.6. Conversion of L-lactide was monitored by comparing the monomer’s methine peak to the methine peak of the polymer and referenced to the internal standard.

A.1.13 Procedure for In Situ Switching Experiments using Catalyst **10_{Zr}**

In a glove box, L-lactide (0.7 mmol), catalyst **10_{Zr}** (0.007 mmol), trimethoxybenzene (internal standard) (0.035 mmol), and CDCl_3 (0.7 mL) were added to a J. Young NMR tube. The NMR tube was sealed and removed from the glove box. The polymerization mixture was heated to 90 °C and monitored by ^1H NMR spectroscopy using a Bruker Avance 400 MHz NMR at 90 °C. The command “multizg” was used to collect data every 10 min. AgBAR^{F} or CoCp_2 (0.007 mmol) were sequentially added to the polymerization solution at the prescribed time interval, and the polymerization mixture was filtered after the addition of AgBAR^{F} to remove precipitate. Conversion of L-lactide was monitored by comparing the monomer’s methine peak to the aromatic peak of the internal standard.

A.1.14 General Polymerization Procedure

In a glove box, L-lactide (1.0 mmol), catalyst (0.01 mmol), and C_6H_6 (1.0 mL) were added to a vial. The mixture was heated with stirring at 90 °C. Polymerization was continued for a prescribed time interval before being

cooled and quenched via exposure of the reaction mixture to air. The solvent was removed in vacuo and the remaining solid was dissolved in dichloromethane and precipitated into methanol to yield PLA as a white solid, which was dried under reduced pressure.

A.2 Supporting Information – Chapter 2

A.2.1 NMR Spectroscopy

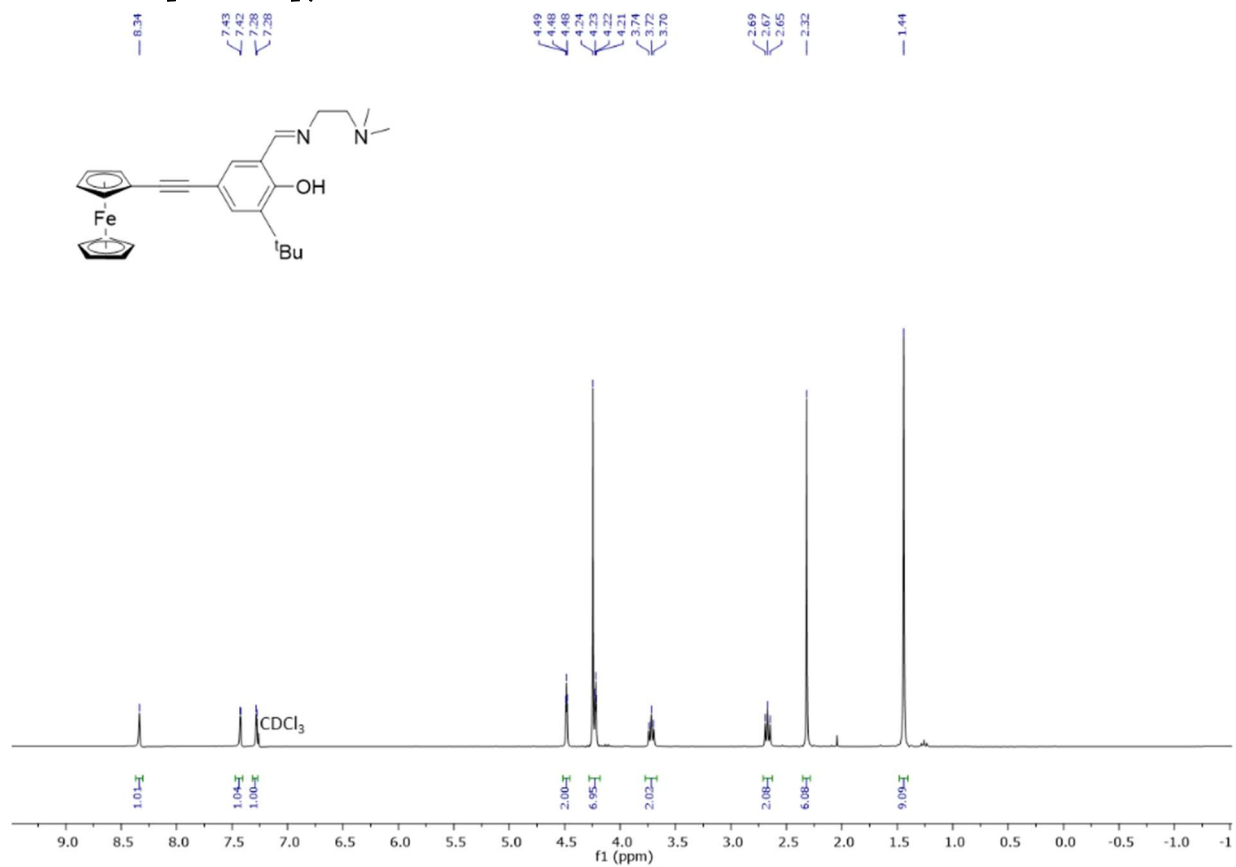


Figure A.1 ^1H NMR (300 MHz, 25°C , CDCl_3) of **L10**, δ , ppm: 1.44 (s, 9H, CH_3), 2.32 (s, 6H, NCH_3), 2.67 (t, 2H, NCH_2), 3.72 (t, 2H, NCH_2), 4.21 (t, 2H, CpH), 4.24 (s, 5H, CpH), 4.48 (t, 2H, CpH), 7.28 (d, 1H, PhH), 7.42 (d, 1H, PhH), 8.34 (s, 1H, NCH).

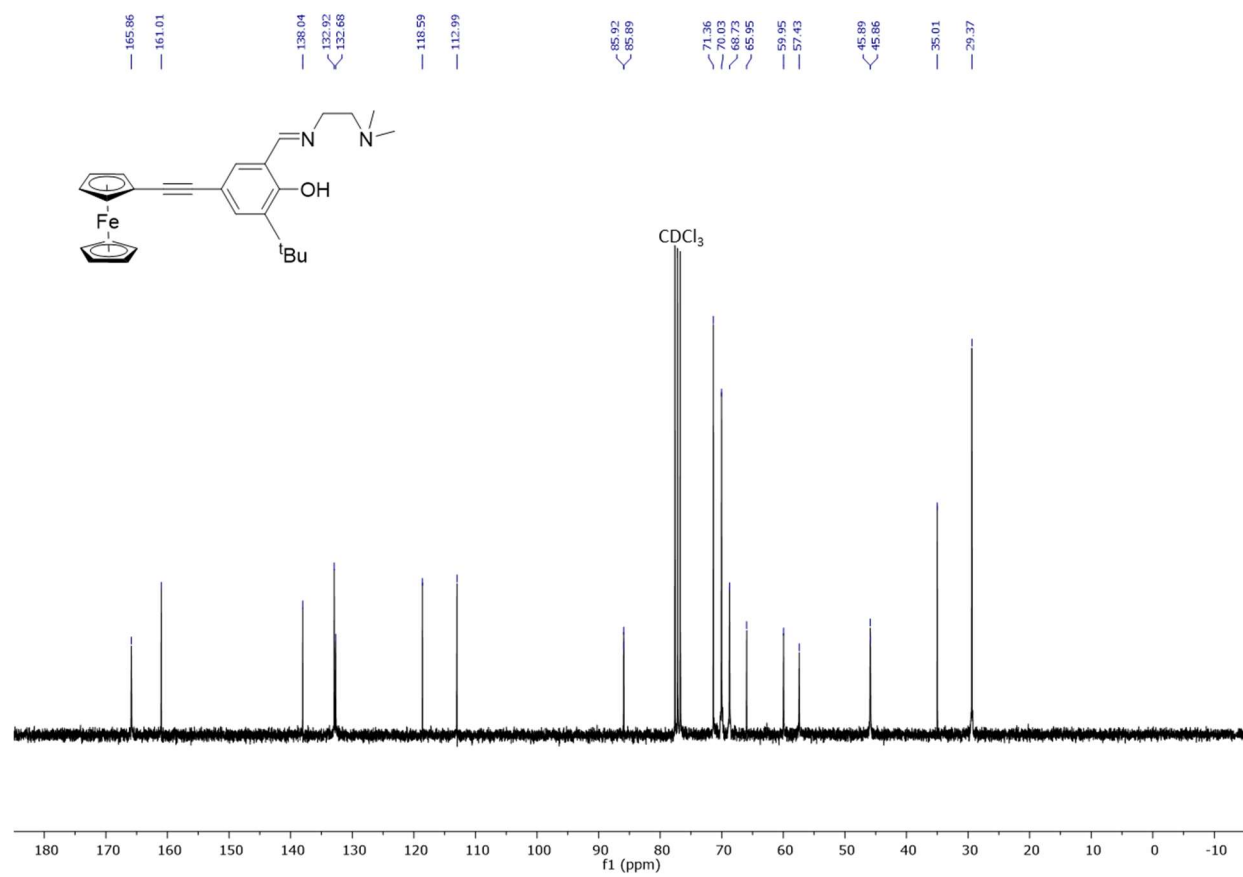


Figure A.2 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of **L10**, δ , ppm: 29.3 ($\text{C}(\text{CH}_3)_3$), 35.0 ($\text{C}(\text{CH}_3)_3$), 45.86 (NCH_3), 45.89 (NCH_3), 57.4 (NCH_2), 59.9 (NCH_2), 65.9 (Cp-C), 68.7 (Cp-C), 70.0 (Cp-C), 71.3 (Cp-C), 85.8 ($\text{C}\equiv\text{C}$), 85.9 ($\text{C}\equiv\text{C}$), 112.9 (aromatic), 118.5 (aromatic), 132.6 (aromatic), 132.9 (aromatic), 138.0 (aromatic), 161.0 (aromatic), 165.8 (NCH).

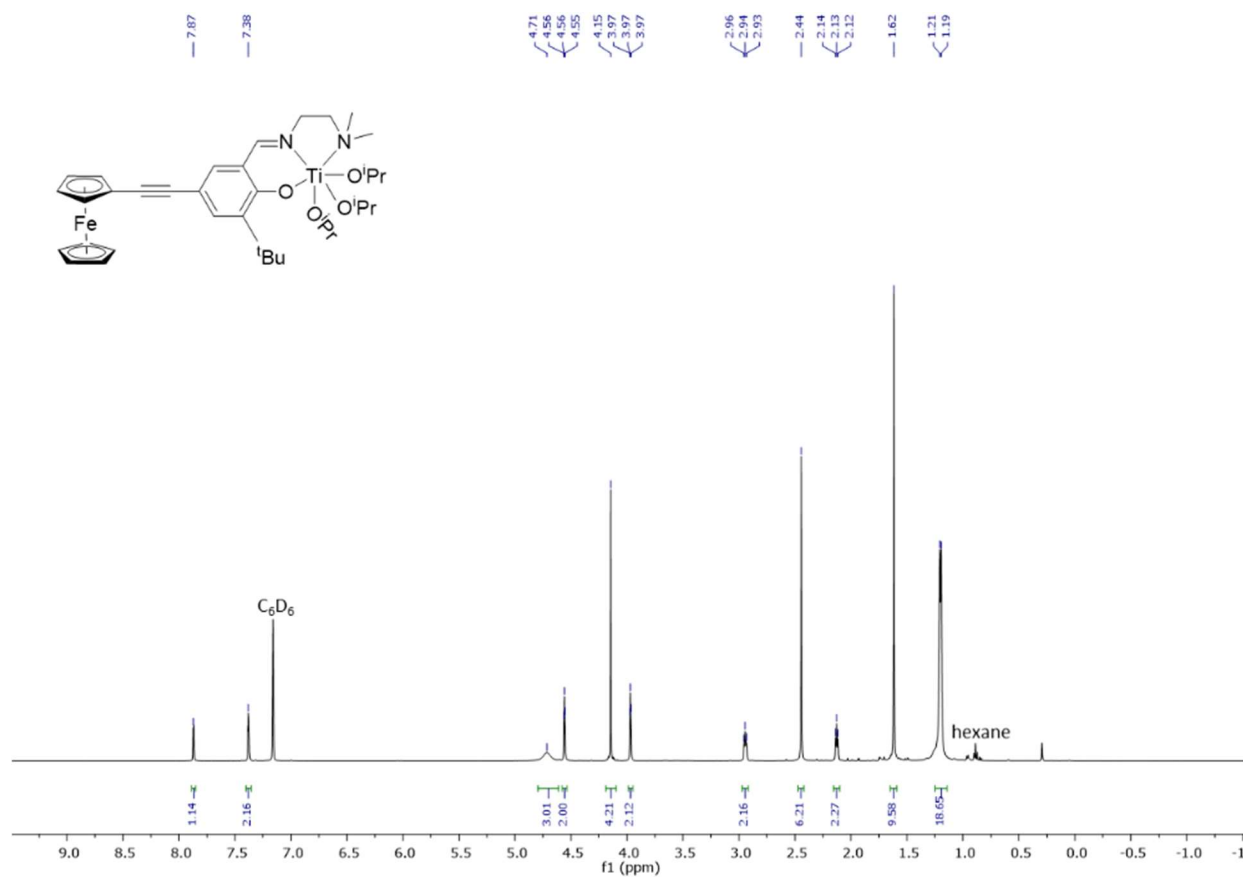


Figure A.3 ^1H NMR (300 MHz, 25 °C, C_6D_6) of **10Ti**, δ , ppm: 1.20 (d, 18H, CH_3), 1.62 (s, 9H, CH_3), 2.13 (t, 2H, NCH_2), 2.44 (s, 6H, NCH_3), 2.94 (t, 2H, NCH_2), 3.97 (t, 2H, CpH), 4.15 (s, 5H, CpH), 4.56 (t, 2H, CpH), 4.71 (br, 3H, OCH), 7.38 (s, 2H, PhH), 7.87 (s, 1H, NCH).

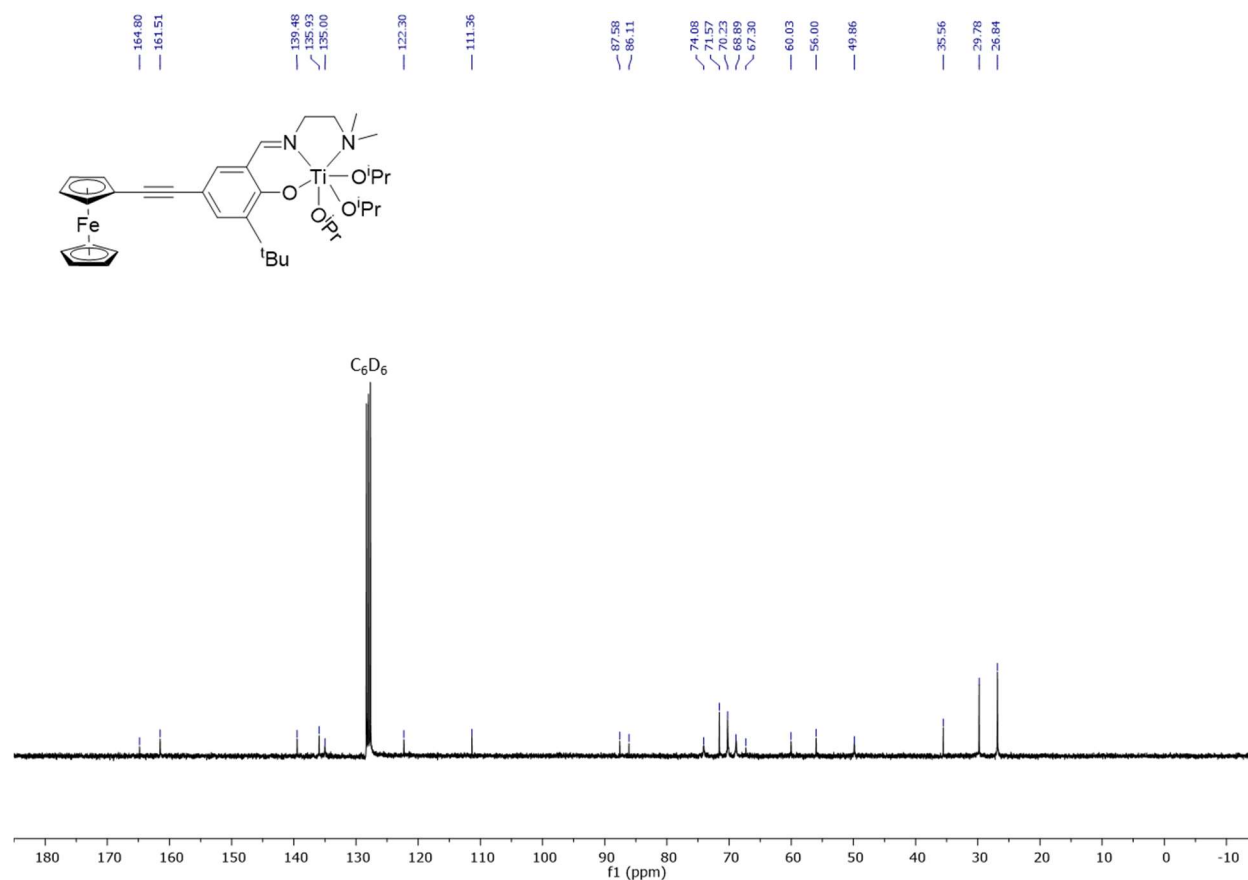


Figure A.4 ¹³C NMR (300 MHz, 25 °C, C₆D₆) of **10_{Ti}**, δ , ppm: 26.8 (CH(CH₃)₂), 29.7 (C(CH₃)₃), 35.5 (C(CH₃)₃), 49.8 (NCH₃), 56.0 (NCH₂), 60.0 (NCH₂), 67.3 (Cp-C), 68.8 (Cp-C), 70.2 (Cp-C), 71.5 (Cp-C), 74.0 (CH(CH₃)₂), 86.1 (C $\equiv$ C), 87.5 (C $\equiv$ C), 111.3 (aromatic), 122.3 (aromatic), 135.0 (aromatic), 135.9 (aromatic), 139.4 (aromatic), 161.5 (aromatic), 164.8 (NCH).

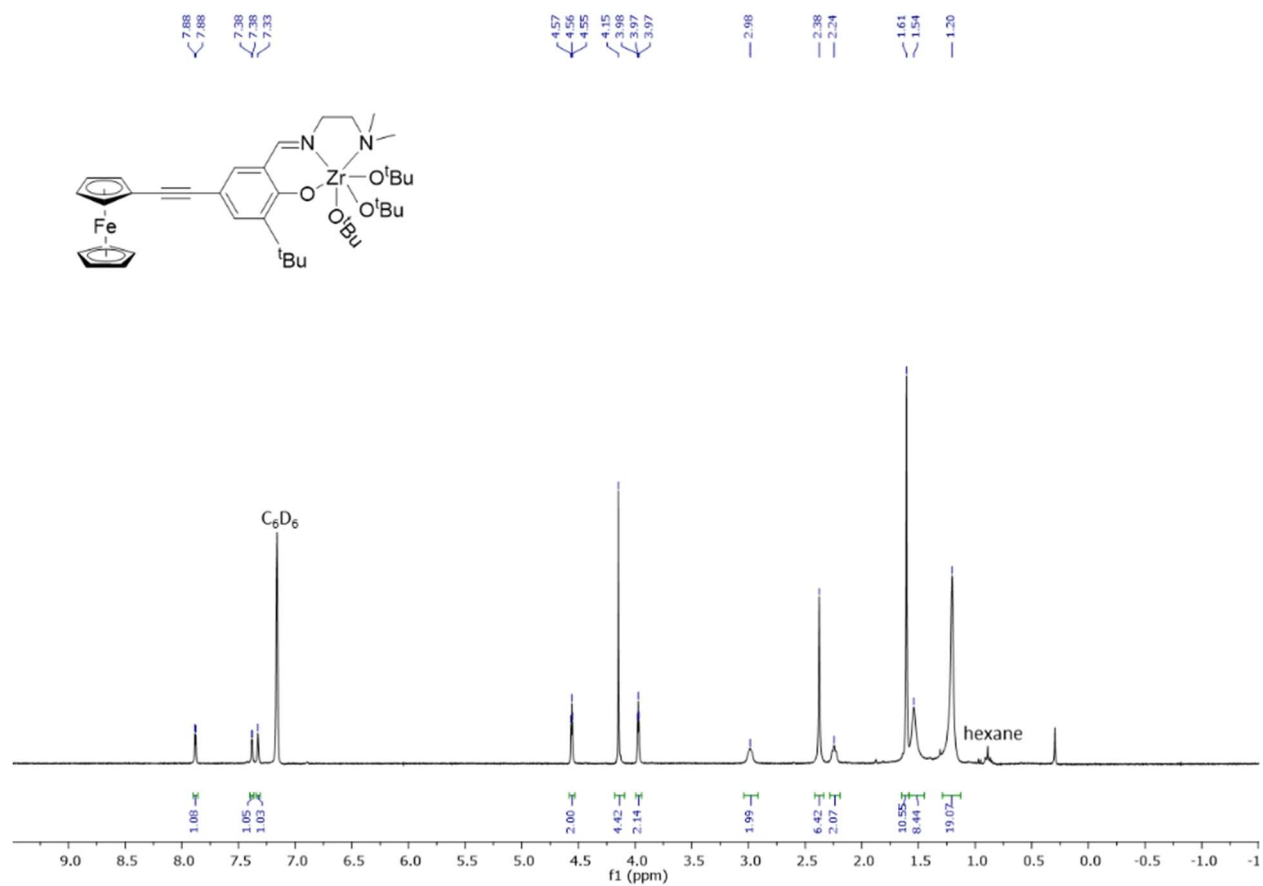


Figure A.5 ¹H NMR (300 MHz, 25 °C, C₆D₆) of **10z**, δ, ppm: 1.20 (s, 18H, CH₃), 1.54 (s, 9H, CH₃), 1.61 (s, 9H, CH₃), 2.24 (t, 2H, NCH₂), 2.38 (s, 6H, NCH₃), 2.98 (t, 2H, NCH₂), 3.97 (t, 2H, CpH), 4.15 (s, 5H, CpH), 4.56 (t, 2H, CpH), 7.33 (s, 1H, PhH), 7.38 (d, 1H, PhH), 7.88 (d, 1H, NCH).

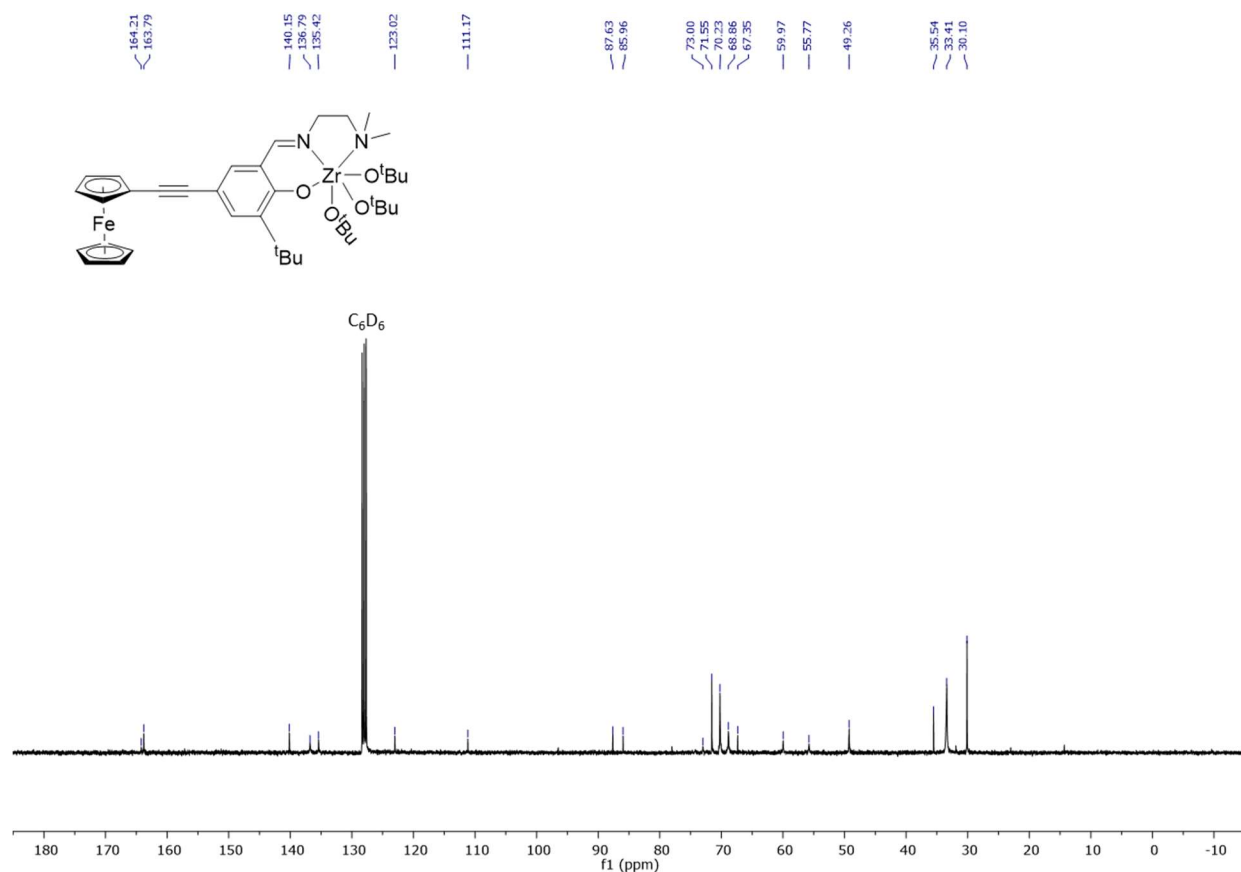


Figure A.6 ¹³C NMR (300 MHz, 25 °C, C₆D₆) of **10_{Zr}**, δ, ppm: 30.1 (OC(CH₃)₃), 33.4 (C(CH₃)₃), 35.5 (C(CH₃)₃), 49.2 (NCH₃), 55.7 (NCH₂), 59.9 (NCH₂), 67.3 (Cp-C), 68.8 (Cp-C), 70.2 (Cp-C), 71.5 (Cp-C), 73.0 (OC(CH₃)₃), 85.9 (C≡C), 87.6 (C≡C), 111.1 (aromatic), 123.0 (aromatic), 135.4 (aromatic), 136.7 (aromatic), 140.1 (aromatic), 163.7 (aromatic), 164.2 (NCH).

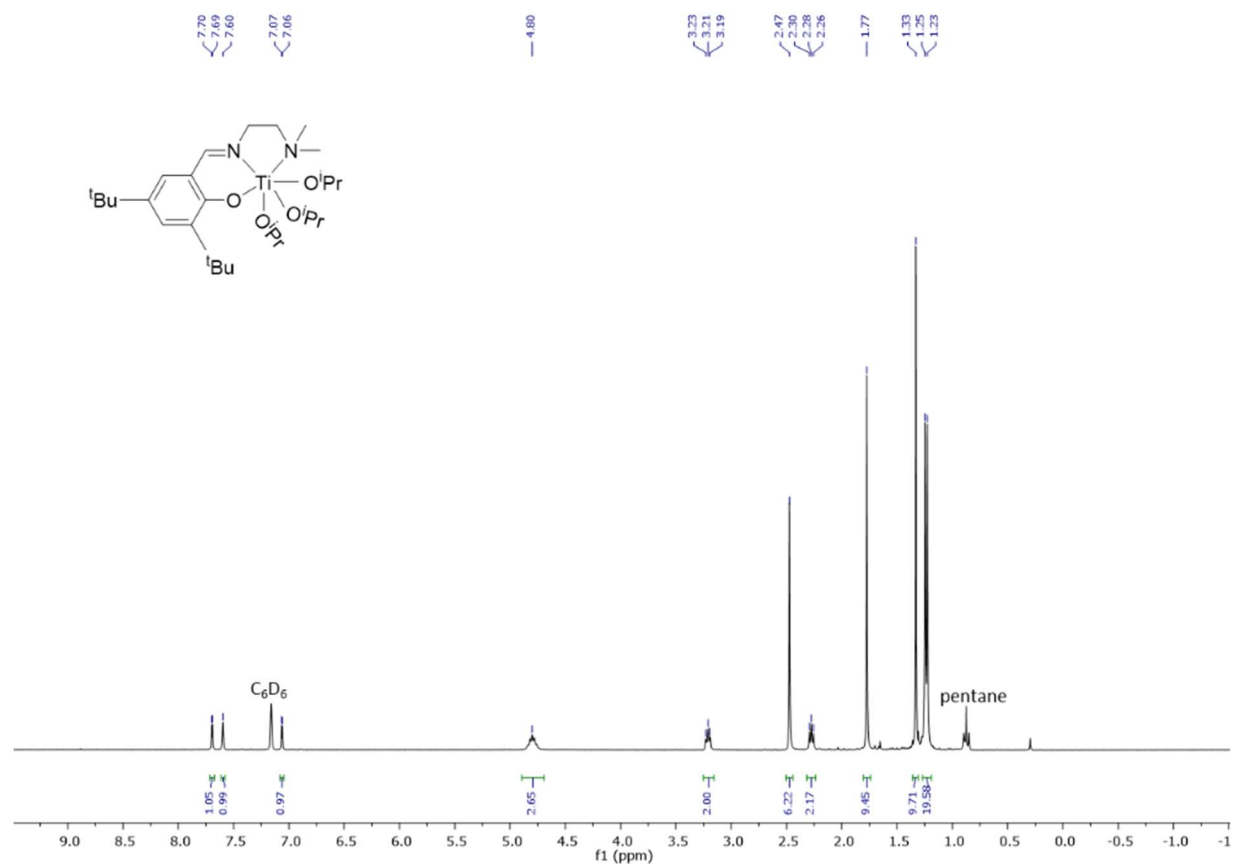


Figure A.7 ¹H NMR (300 MHz, 25 °C, C₆D₆) of **11_{Ti}**, δ, ppm: 1.23 (d, 18H, CH₃), 1.33 (s, 9H, CH₃), 1.77 (s, 9H, CH₃), 2.28 (t, 2H, NCH₂), 2.47 (s, 6H, CH₃), 3.21 (t, 2H, NCH₂), 4.80 (m, 3H, CH), 7.06 (d, 1H, PhH), 7.60 (s, 1H, NCH), 7.70 (d, 1H, PhH).

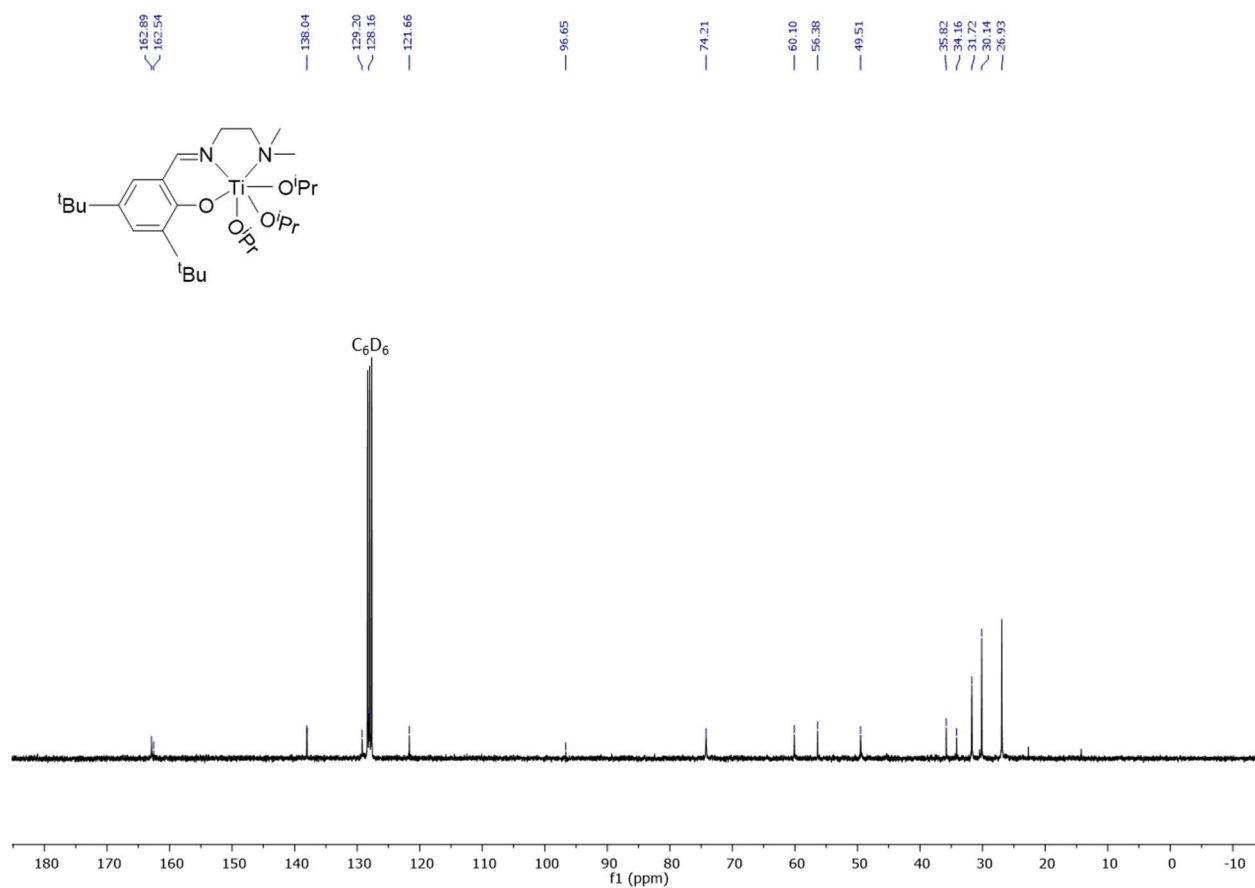


Figure A.8 ¹³C NMR (300 MHz, 25 °C, C₆D₆) of **11-Ti**, δ, ppm: 26.9 (OCH(CH₃)₂), 30.1 (C(CH₃)₃), 31.7 (C(CH₃)₃), 34.1 (C(CH₃)₃), 35.8 (C(CH₃)₃), 49.5 (NCH₃), 56.3 (NCH₂), 60.1 (NCH₂), 74.2 (C(CH₃)₂), 96.6 (aromatic), 121.6 (aromatic), 128.1 (aromatic), 129.2 (aromatic), 138.0 (aromatic), 162.5 (aromatic), 162.8 (NCH).

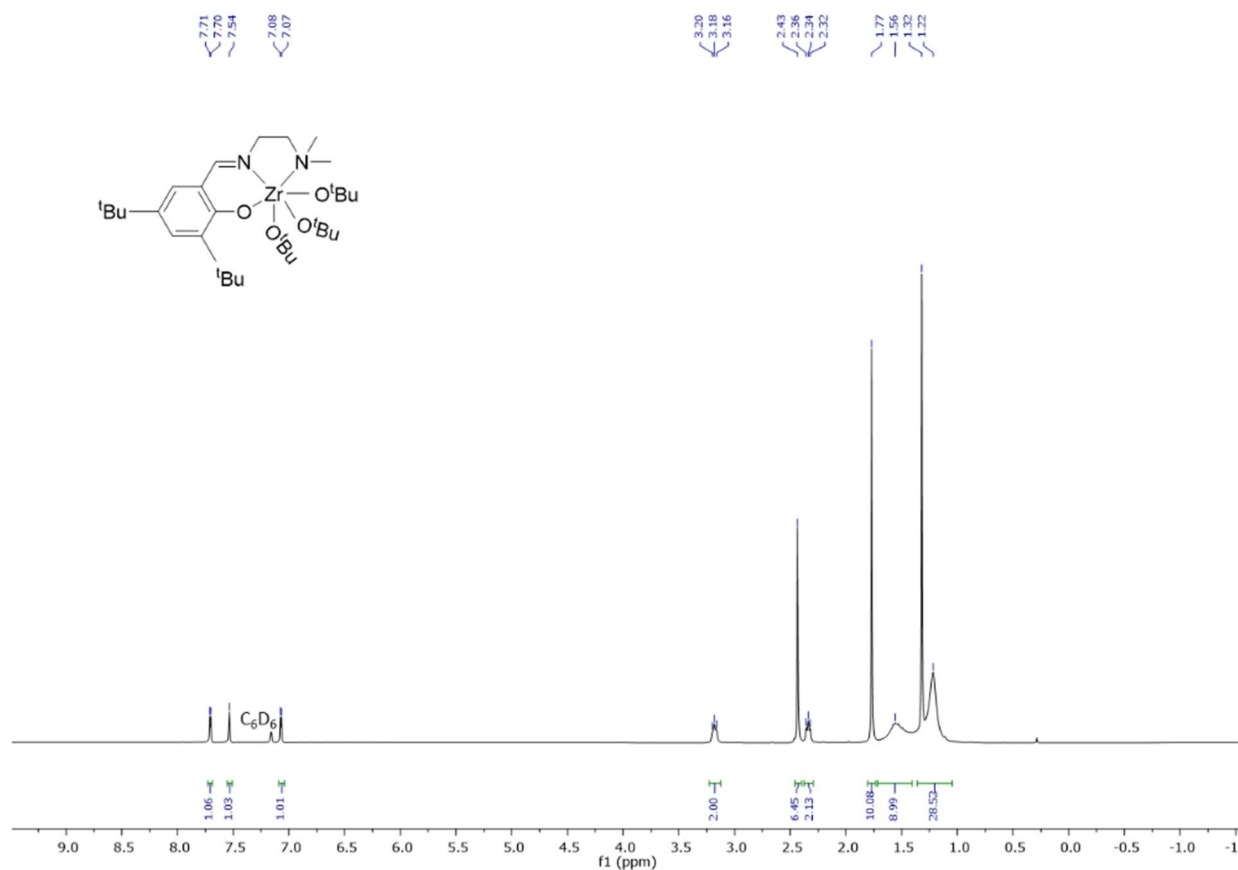


Figure A.9 ^1H NMR (300 MHz, 25°C , C_6D_6) of **11z**, δ , ppm: 1.22 (br, 18H, $\text{OC}(\text{CH}_3)_3$), 1.32 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.56 (br, 9H, $\text{OC}(\text{CH}_3)_3$), 1.77 (s, 9H, $\text{C}(\text{CH}_3)_3$), 2.34 (t, 2H, NCH_2), 2.43 (s, 6H, NCH_3), 3.18 (t, 2H, NCH_2), 7.08 (d, 1H, PhH), 7.54 (s, 1H, NCH), 7.71 (d, 1H, PhH).

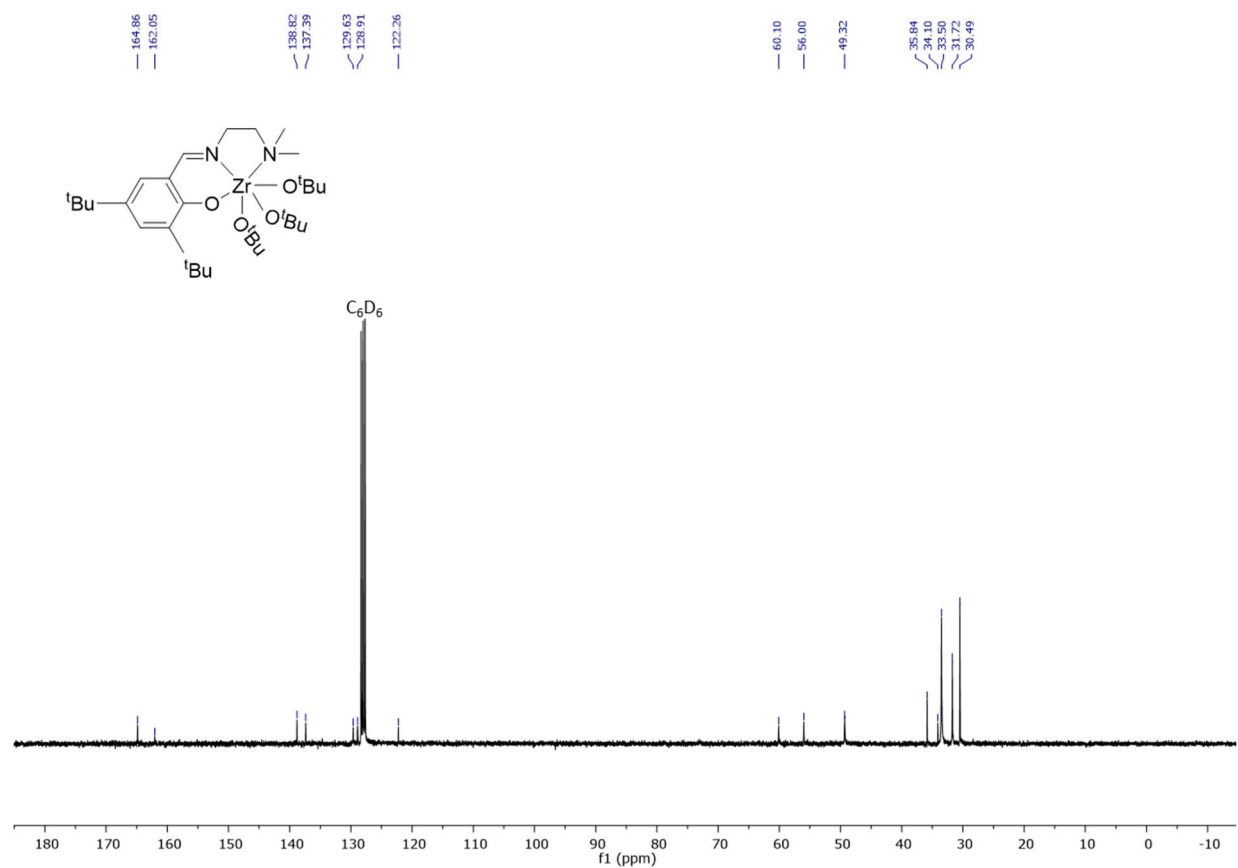


Figure A.10 ¹³C NMR (300 MHz, 25 °C, C₆D₆) of **11_{Zr}**, δ, ppm: 30.4 (OC(CH₃)₃), 31.7 (C(CH₃)₃), 33.5 (C(CH₃)₃), 34.1 (C(CH₃)₃), 35.8 (C(CH₃)₃), 49.3 (NCH₃), 56.0 (NCH₂), 60.1 (NCH₂), 122.2 (aromatic), 128.9 (aromatic), 129.6 (aromatic), 137.3 (aromatic), 138.8 (aromatic), 162.0 (aromatic), 164.8 (NCH).

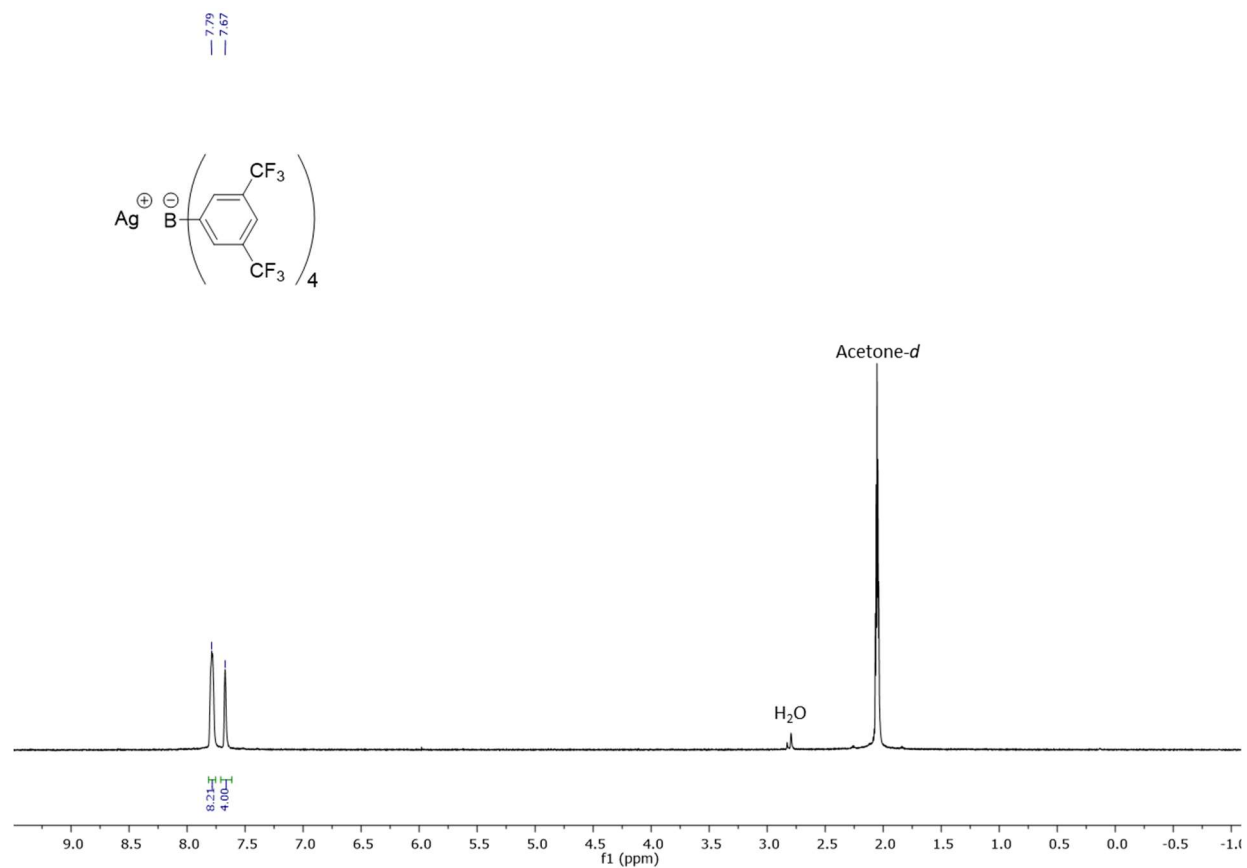


Figure A.11 ^1H NMR (300 MHz, 25 °C, acetone- d_6) of AgBAR^{F} , δ , ppm: 7.67 (s, 4H, aromatic), 7.79 (s, 8H, aromatic).

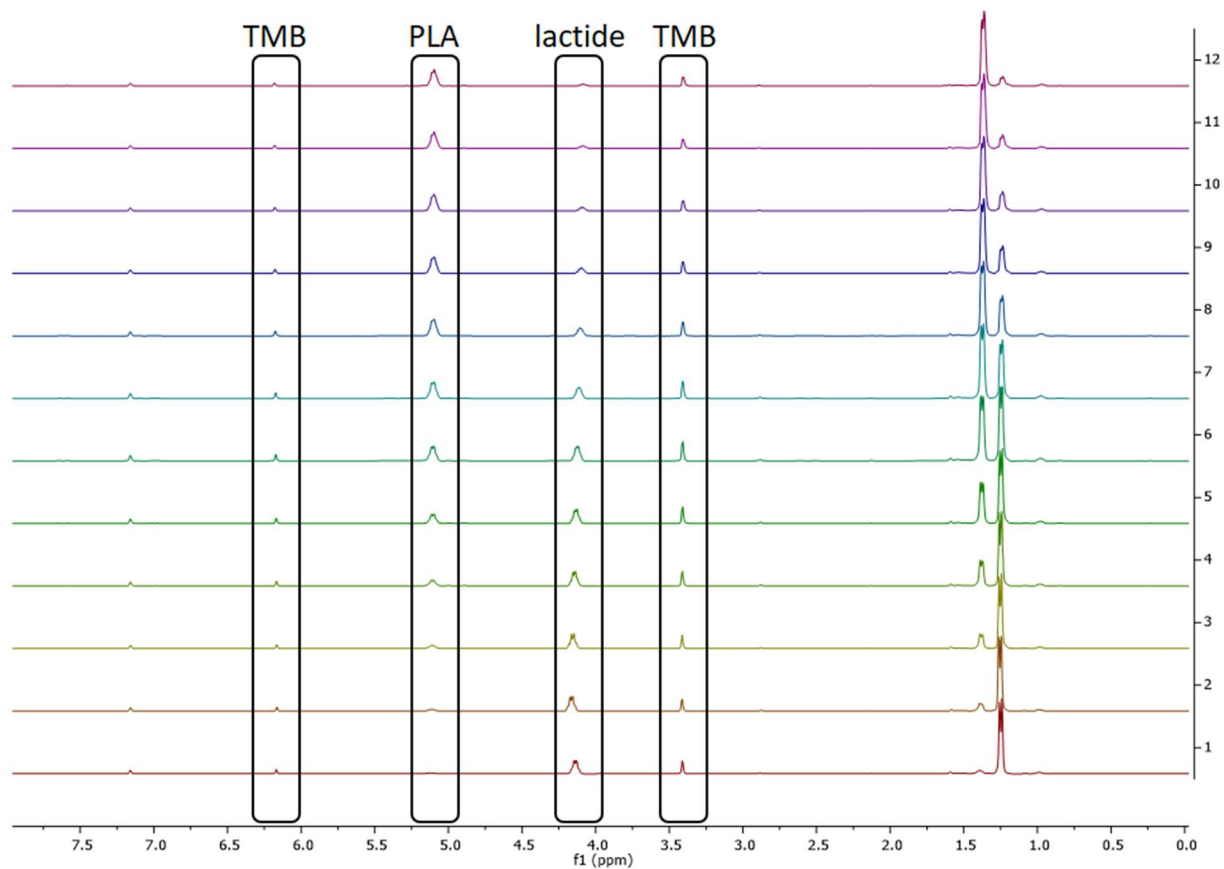


Figure A.12 ^1H NMR spectra (400 MHz, 90°C , C_6D_6) monitoring the polymerization of L-LA initiated by catalyst **11_{Ti}**. Each trace represents an hourly progression of the reaction starting at 1 hour and ending at 12 hours. The bottom trace (1 hour) shows a large presence of L-LA with little to no polymer. The top trace (12 hours) shows L-LA has been mostly converted to polylactide (PLA). Throughout the 12 hours the amount of internal standard (trimethoxybenzene (TMB)) remained constant.

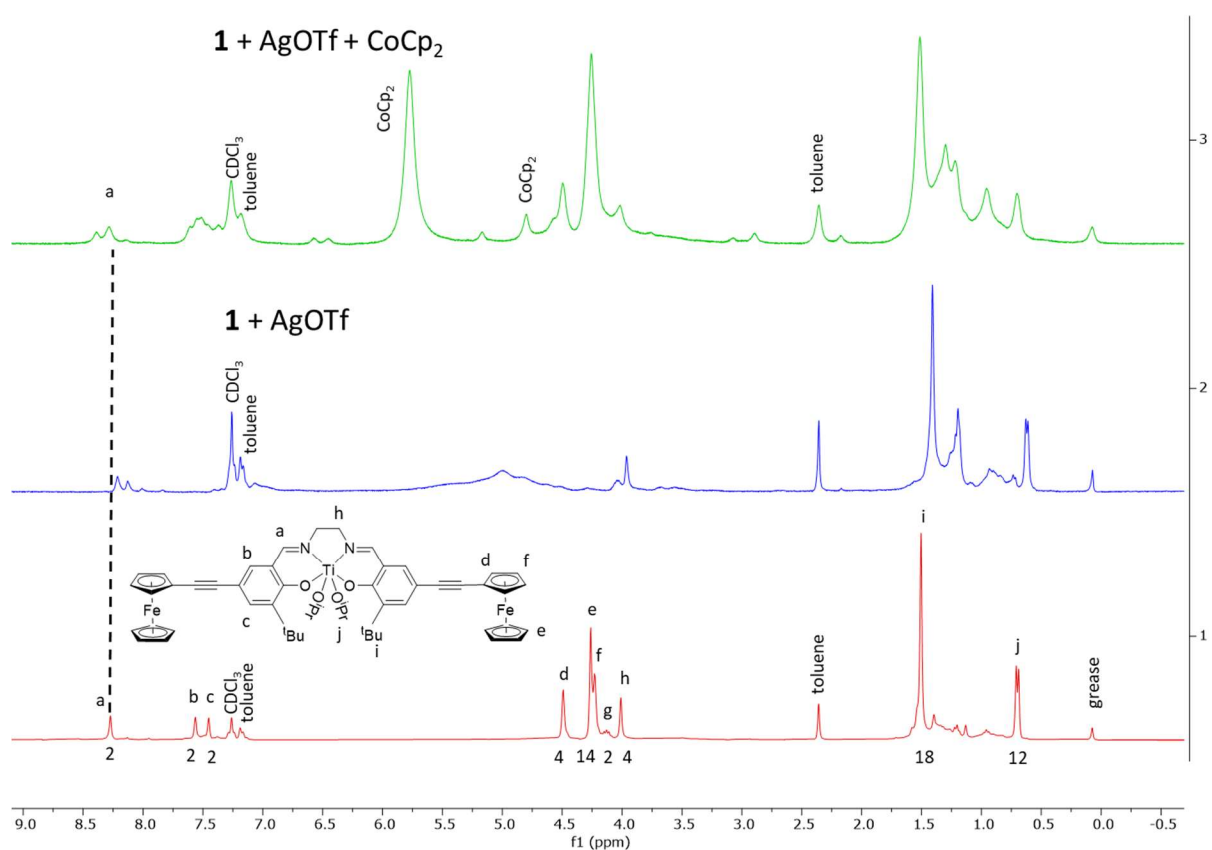


Figure A.13 ^1H NMR spectra (300 MHz, 25 °C, CDCl_3) of **1** (bottom), **1_{ox}** (middle), and **1_{red}** (top). **1_{ox}** was generated by the addition of 2 equivalence of AgOTf to **1** in CDCl_3 in a J. Young NMR tube. **1_{red}** was generated by the subsequent addition of CoCp_2 to the NMR tube. A shift in the peaks is seen between the bottom and middle spectra. Another shift in the peaks is seen between the middle and top spectra but the peaks in the top spectrum do not shift back to the same position as the peaks in the bottom spectrum.

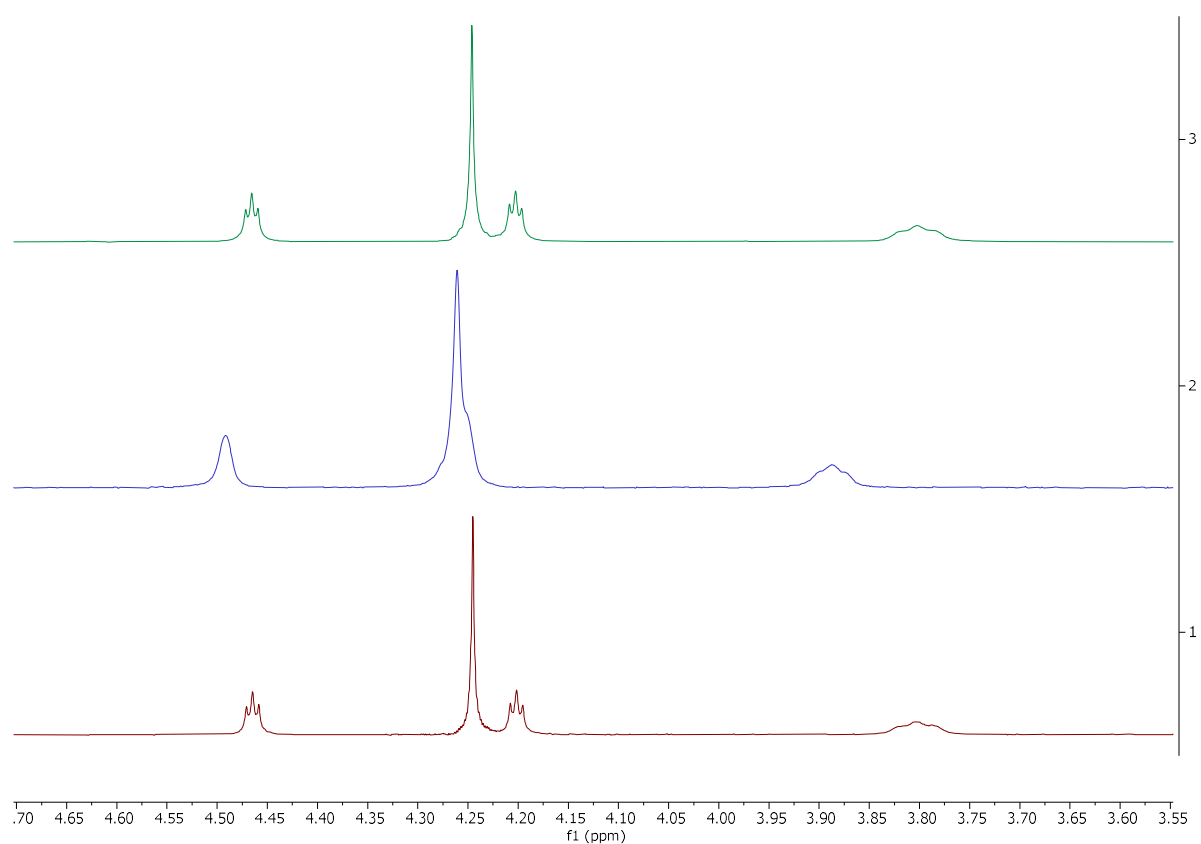


Figure A.14 Zoomed in ^1H NMR spectra (300 MHz, 25 $^\circ\text{C}$, CDCl_3) of **10_{Zr}** (bottom), **10_{Zr-ox}** (middle), and **10_{Zr-red}** (top). **10_{Zr-ox}** was generated by the addition of AgBAR^{F} to **10_{Zr}** in CDCl_3 followed heating at 90 $^\circ\text{C}$ for 1 h in a J. Young NMR tube. **10_{Zr-red}** was generated by the addition of AgBAR^{F} to **10_{Zr}** in CDCl_3 followed by filtration into a new vial with CoCp_2 then addition to the NMR tube. A broadening as well as a shift in the ferrocenyl peaks is seen between the bottom and middle spectra. Another shift in the peaks is seen between the middle and top spectra with the peaks in the top spectrum shifting back to the same position as the peaks in the bottom spectrum.

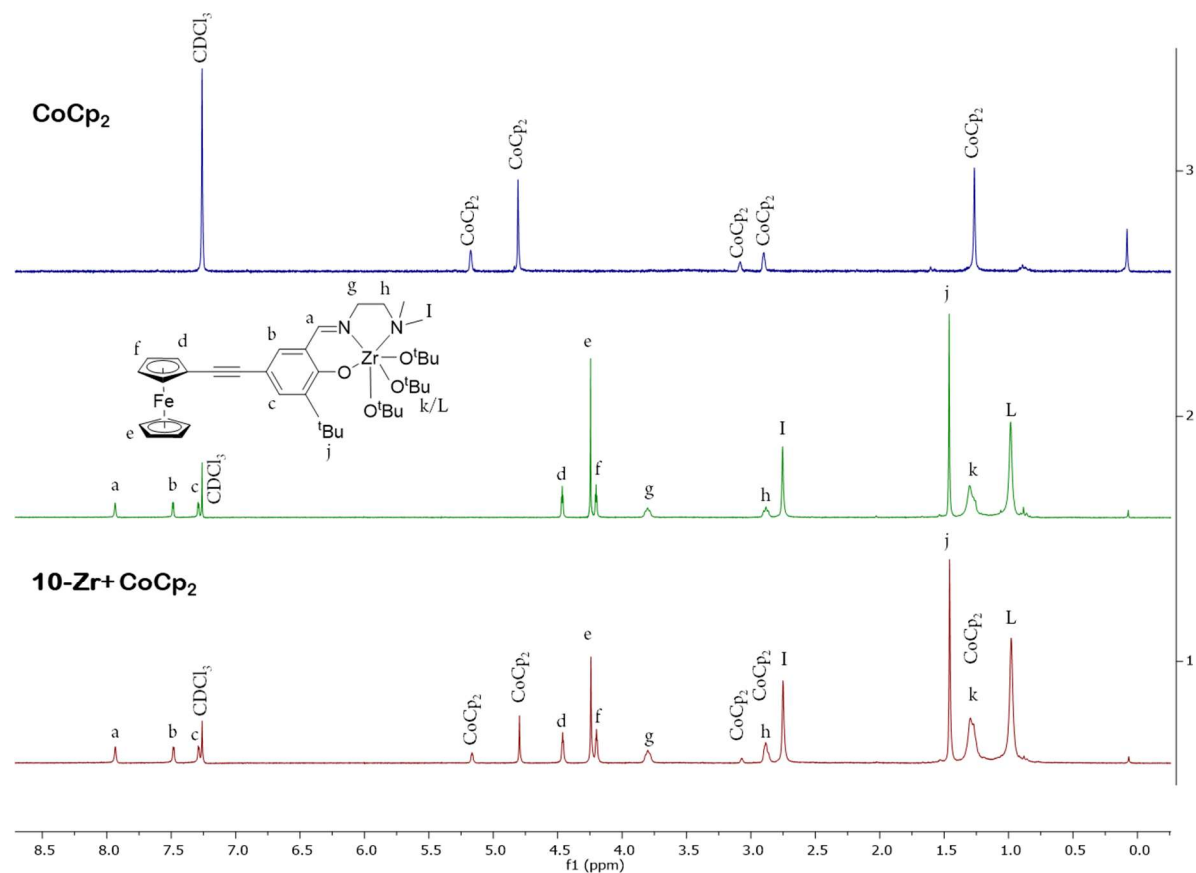


Figure A.15 ^1H NMR spectra (300 MHz, 25 $^\circ\text{C}$, CDCl_3) of $\mathbf{10-Zr}$ + 1.2 eq. CoCp_2 (bottom), $\mathbf{10-Zr}$ (middle), and CoCp_2 (top). Every peak in the bottom spectrum can be accounted for from either the middle or top spectra indicating that the CoCp_2 has no direct effect on $\mathbf{10-Zr}$.

A.2.2 Polymerization Data

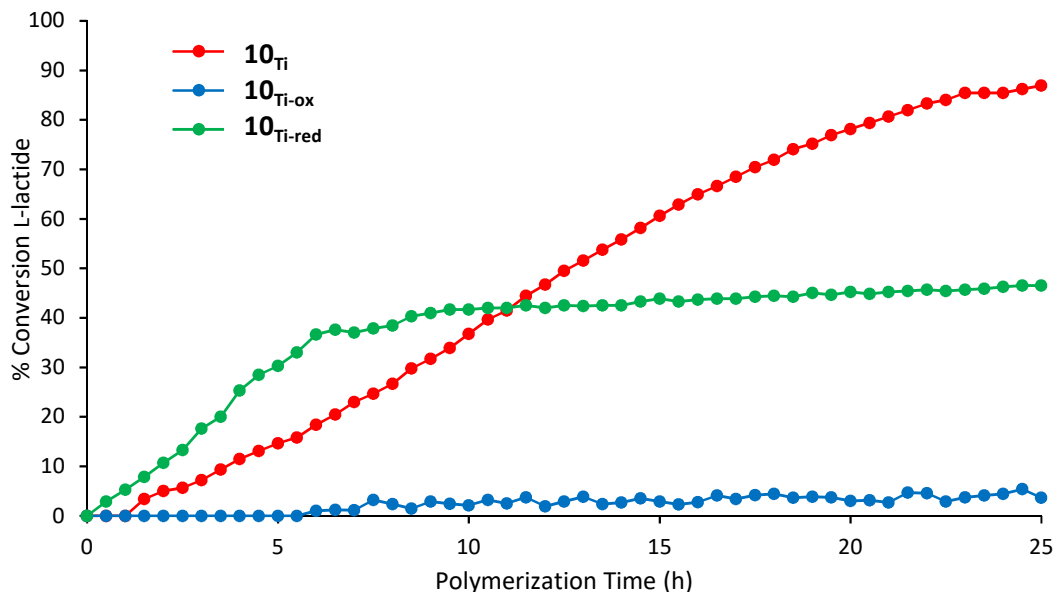


Figure A.16 Plot of monomer conversion (%) versus time (h) for the polymerization of L-LA (100 eq, 1M) in CDCl₃ at 90 °C using 10_{Ti} (red circles), 10_{Ti-ox} (blue circles), and 10_{Ti-red} (green circles). Using AgBAR^F as an oxidizing agent and CoCp₂ as a reducing agent.

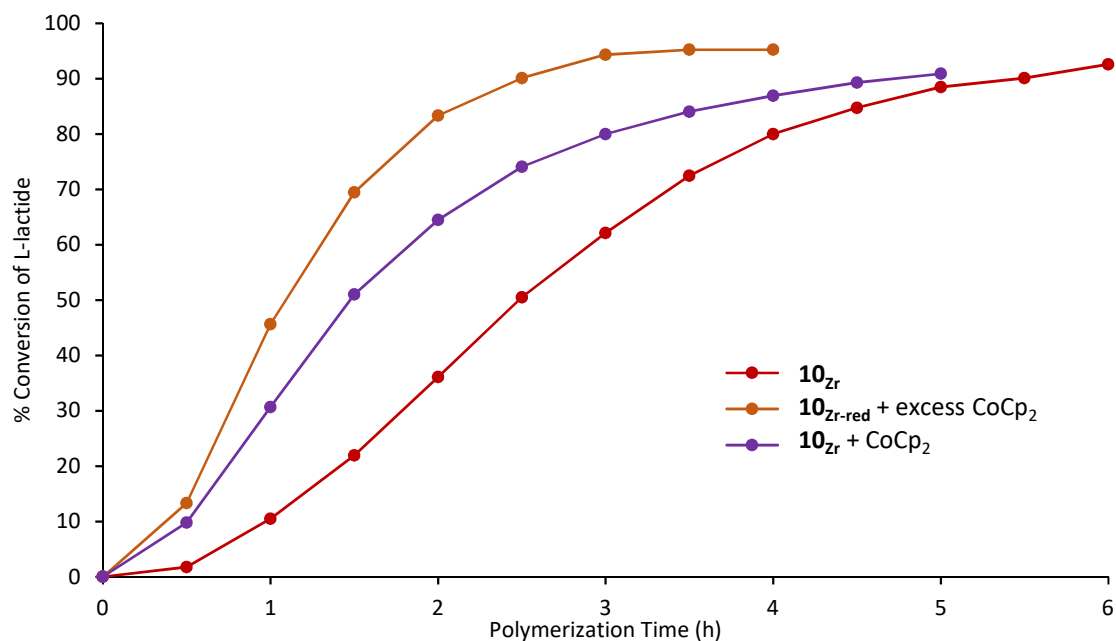


Figure A.17 Plot of monomer conversion (%) versus time (h) for the polymerization of L-LA (100 eq, 1 M) in CDCl₃ at 90 °C using 10_{Zr} (red circles), 10_{Zr} + 1 eq. CoCp₂ (purple circles), and 10_{Zr-red} generated with excess (1.5 eq.) CoCp₂ (orange circles).

A.2.3 Cyclic Voltammetry

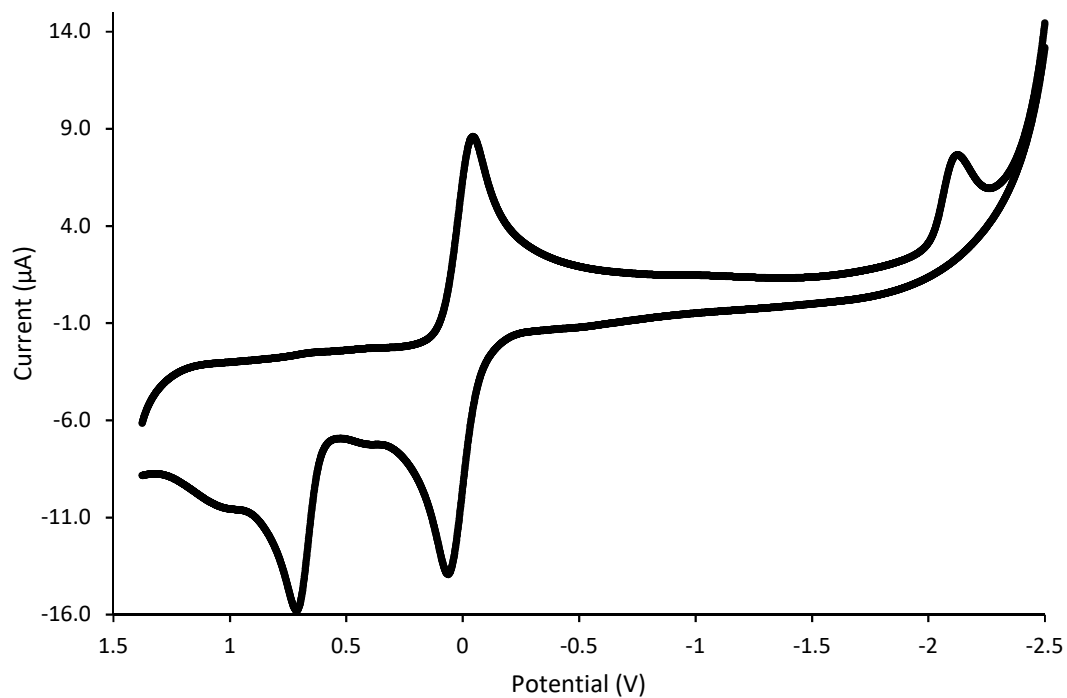


Figure A.18 Cyclic voltammogram of catalyst **10_{Zr}** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (nBu)₄NPF₆ (0.20 M), ($E_{1/2}$ = 0.03 V) versus Fc/Fc⁺.

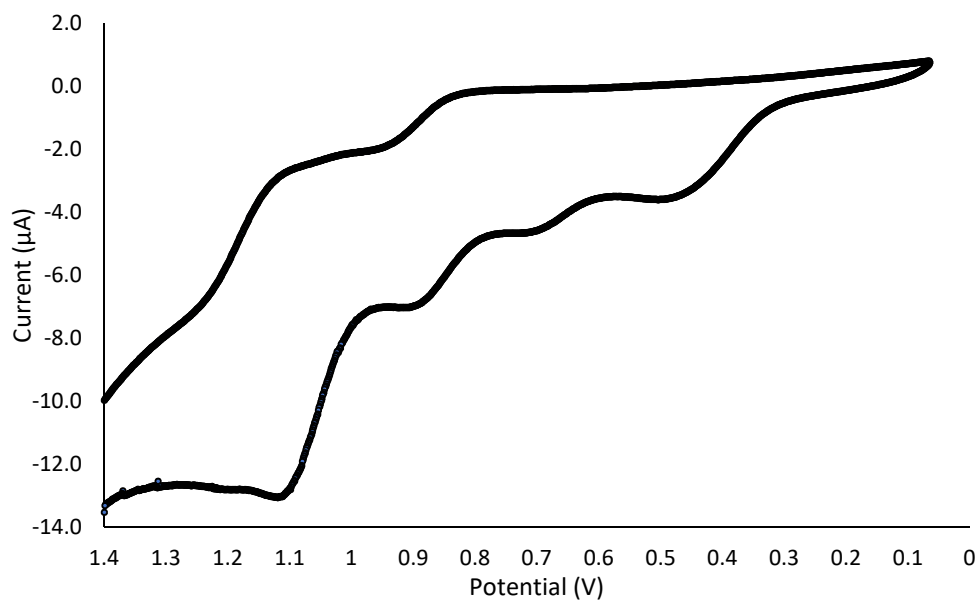


Figure A.19 Cyclic voltammogram of catalyst **11_{Ti}** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (nBu)₄NPF₆ (0.20 M).

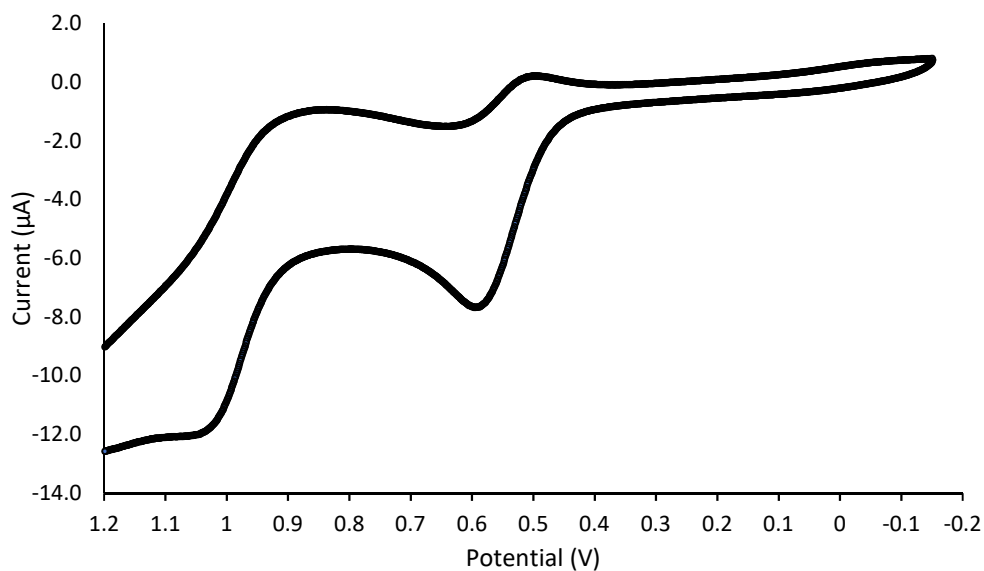


Figure A.20 Cyclic voltammogram of catalyst **11_{Zr}** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (nBu)₄NPF₆ (0.20 M).

A.2.4 UV-vis Spectra

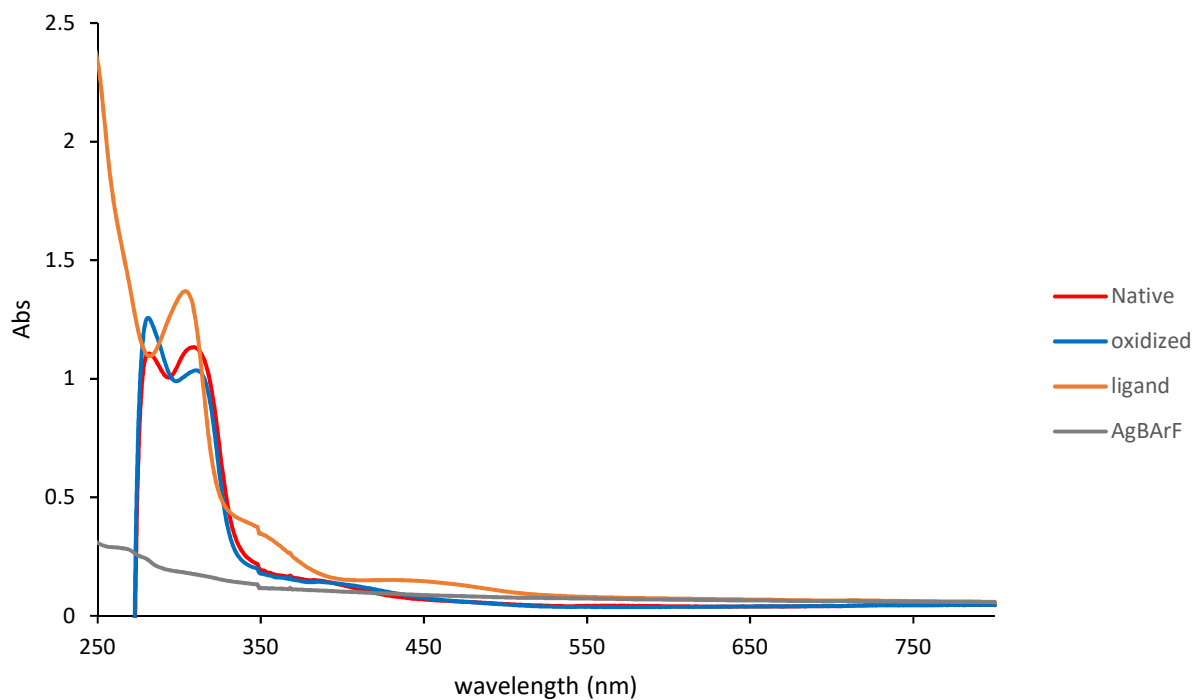


Figure A.21 UV-Vis Spectra of **10_{Zr}** (4.2×10^{-5} M) (red), **10_{Zr-ox}** (4.2×10^{-5} M) (blue), **L10** (4.2×10^{-5} M) (orange), and AgBARF (4.2×10^{-5} M) (gray).

A.2.5 X-ray Crystallographic Data

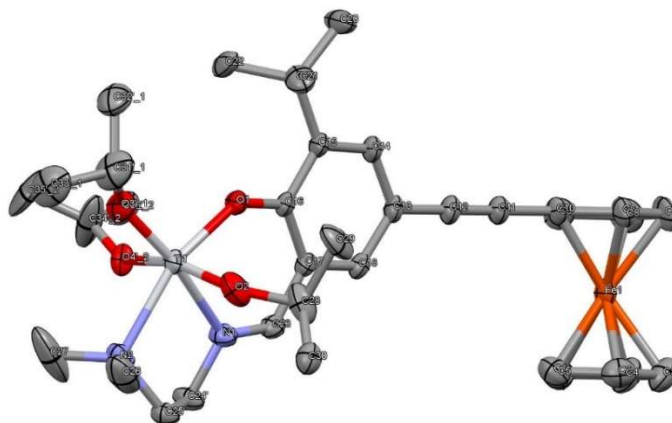


Figure A.22 ShelXle representation of **10_{Ti}** with thermal ellipsoids drawn at 50% probability. Hydrogens were omitted for clarity. X-ray quality single crystals of **10_{Ti}** were obtained via recrystallization from hexanes upon cooling to -20 °C. Crystal data for C₃₆H₅₅FeN₂O₄Ti (680.53 g/mol); monoclinic; space group P2(1)/c; a= 22.6283(13) Å; b= 8.7736(5) Å; c= 18.5643(10) Å; α= 90°; β= 105.170(2)°; γ= 90°; V = 3557.2(3) Å³; Z = 2; T = 100(2) K; λ= 0.71073 Å; μ= 0.670 mm⁻¹; R1= 0.0496; wR2= 0.1381 for 44,451 reflections; GOF = 1.027. CCDC Reference Number: 1993768

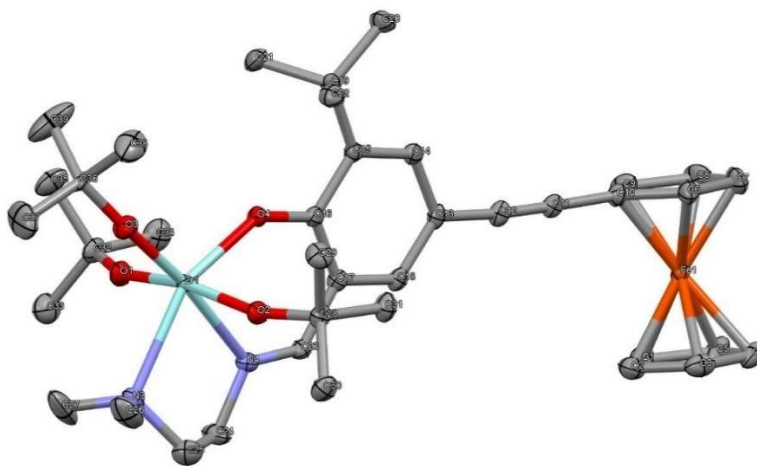


Figure A.23 ShelXle representation of **10_{Zr}** with thermal ellipsoids drawn at 50% probability. Hydrogens were omitted for clarity. X-ray quality single crystals of **10_{Zr}** were obtained via recrystallization from hexanes upon cooling to -20 °C. Crystal data for C₃₉H₅₈FeN₂O₄Zr (765.97 g/mol); monoclinic; space group P2(1)/c; a= 22.8642(12) Å; b= 9.1582(5) Å; c= 19.4463(10) Å; α= 90°; β= 106.4470(10)°; γ= 90°; V = 3905.3(4) Å³; Z = 4; T = 100(2) K; λ= 0.71073 Å; μ= 0.677 mm⁻¹; R1= 0.0353; wR2= 0.0841 for 51,591 reflections; GOF = 1.011. CCDC Reference Number: 1993769

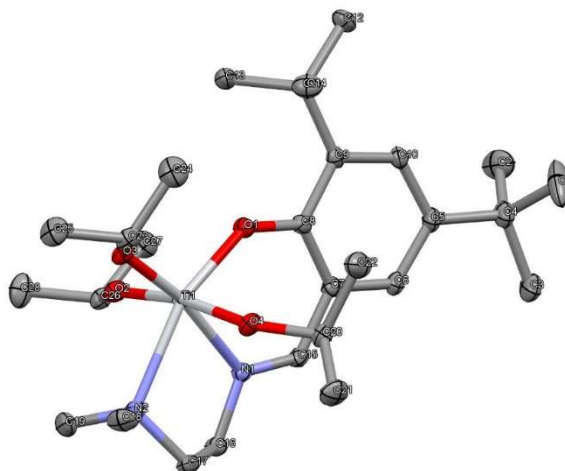


Figure A.24 ShelXle representation of **11_{Ti}** with thermal ellipsoids drawn at 50% probability. Hydrogens and pentane molecules were omitted for clarity. X-ray quality single crystals of **11_{Ti}** were obtained via recrystallization from a concentrated pentanes solution upon cooling to -20 °C. Crystal data for C₂₈H₅₂N₂O₄Ti (528.60 g/mol); monoclinic; space group P2(1)/c; a= 26.1034(16) Å; b= 13.6068(8) Å; c= 18.7389(11) Å; α= 90°; β= 90.427(2)°; γ= 90°; V = 6655.6(7) Å³; Z = 14; T = 100(2) K; λ= 0.71073 Å; μ= 0.290 mm⁻¹; R1= 0.0656; wR2= 0.1482 for 202,143 reflections; GOF = 1.185. CCDC Reference Number: 1993770

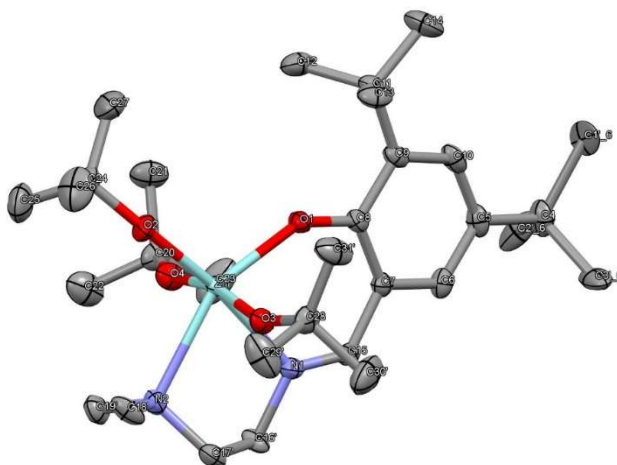


Figure A.25 ShelXle representation of **11_{Zr}** with thermal ellipsoids drawn at 50% probability. Hydrogens were omitted for clarity. X-ray quality single crystals of **11_{Zr}** were obtained via recrystallization from a concentrated pentanes solution upon cooling to -20 °C. Crystal data for C₃₁H₅₈N₂O₄Zr (614.04 g/mol); triclinic; space group P-1; a= 9.0808(8) Å; b= 9.9464(8) Å; c= 21.5037(18) Å; α= 93.147(3)°; β= 91.175(3)°; γ= 115.995(2)°; V = 1741.0(3) Å³; Z = 2; T = 100(2) K; λ= 0.71073 Å; μ= 0.349 mm⁻¹; R1= 0.0459; wR2= 0.1051 for 60,166 reflections; GOF = 0.918. CCDC Reference Number: 1993771

A.2.6 GPC Analysis of Polymers

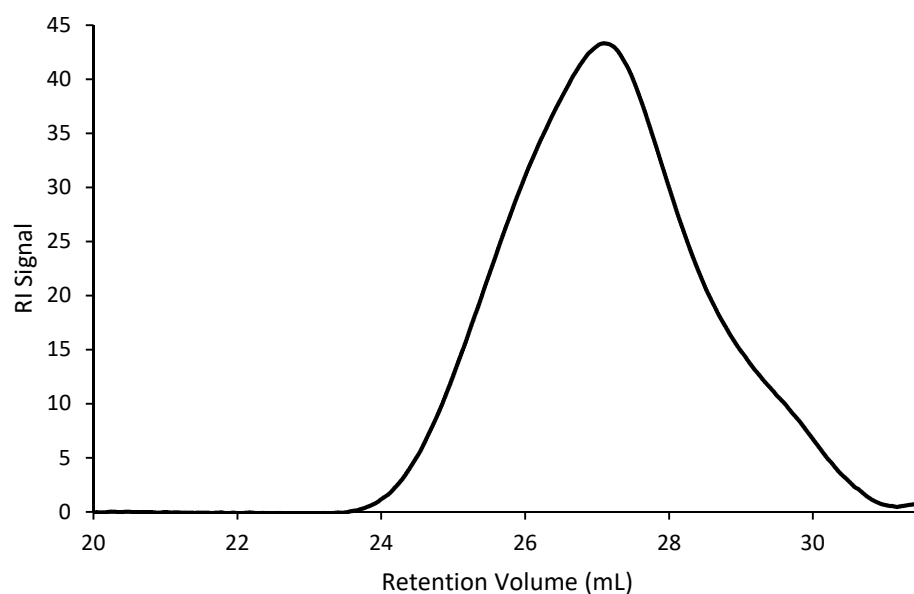


Figure A.26 GPC trace of PLA obtained using **10_{Ti}**. Samples measured in THF at 30 °C and reported as absolute molecular weights (**Table 2.1**, Entry 1).

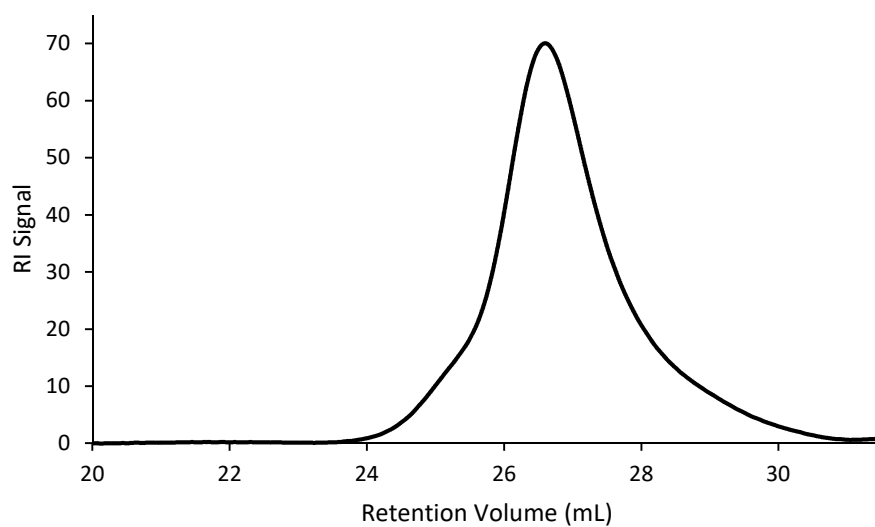


Figure A.27 GPC trace of PLA obtained using **10_{Zr}**. Samples measured in THF at 30 °C and reported as absolute molecular weights (**Table 2.1**, Entry 2).

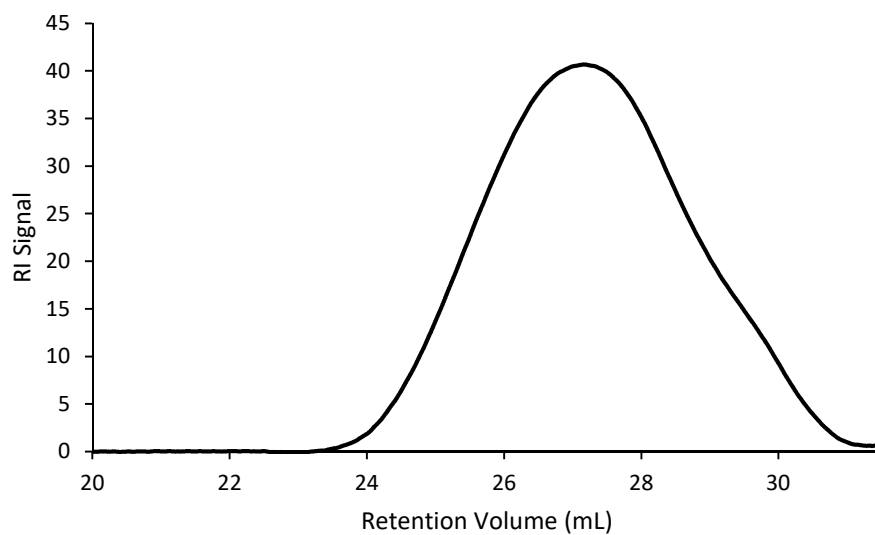


Figure A.28 GPC trace of PLA obtained using **11_{Ti}**. Samples measured in THF at 30 °C and reported as absolute molecular weights (**Table 2.1**, Entry 3).

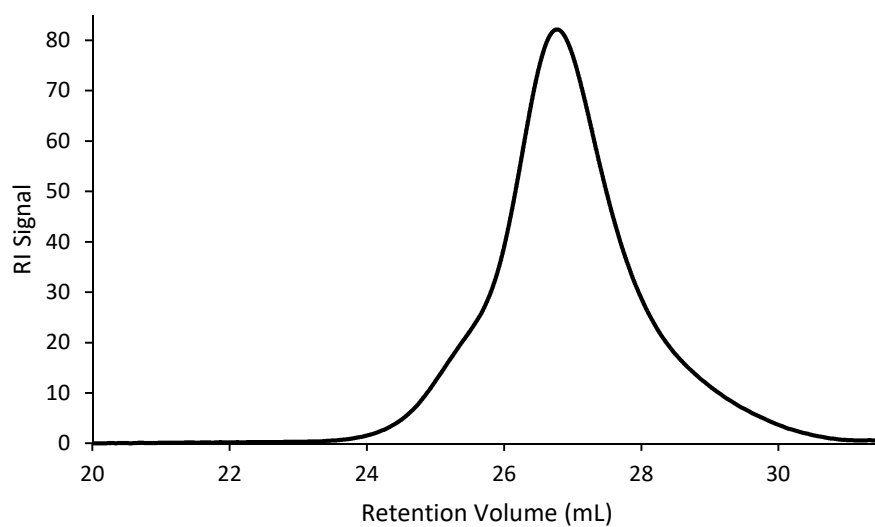


Figure A.29 GPC trace of PLA obtained using **11_{Zr}**. Samples measured in THF at 30 °C and reported as absolute molecular weights (**Table 2.1**, Entry 4).

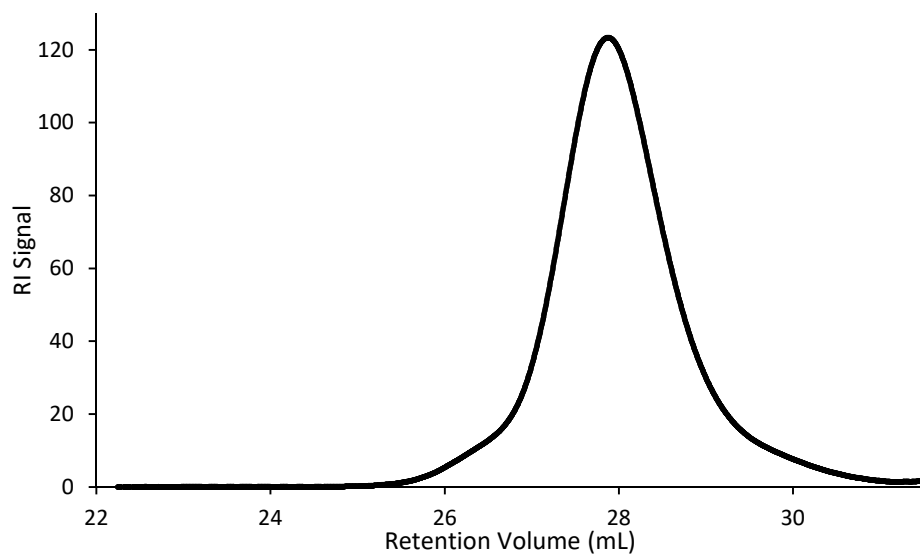


Figure A.30 GPC trace of PLA obtained using **10_{Ti-red}**. Samples measured in THF at 30 °C and reported as absolute molecular weights.

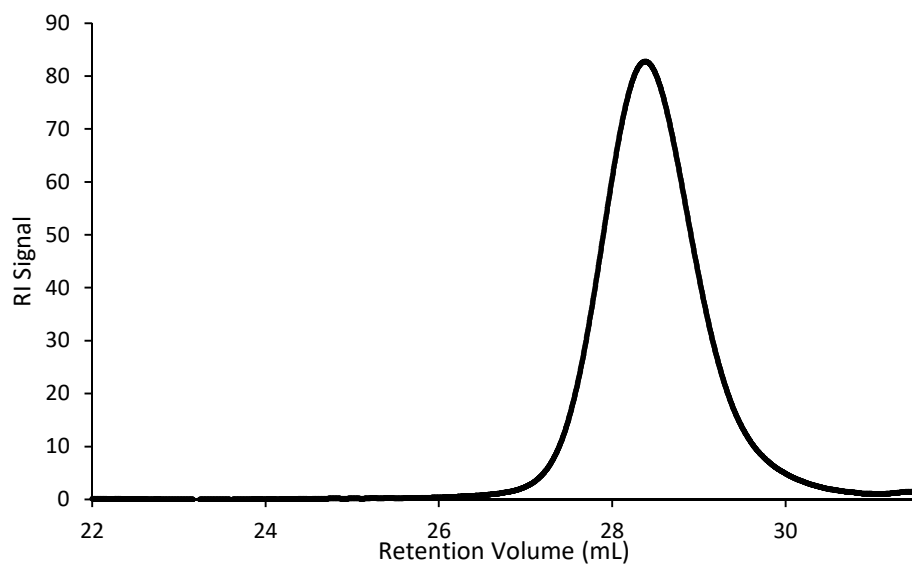


Figure A.31 GPC trace of PLA obtained using **10_{Zr-red}**. Samples measured in THF at 30 °C and reported as absolute molecular weights.

A.2.7 Kinetic Study of L-lactide Polymerization

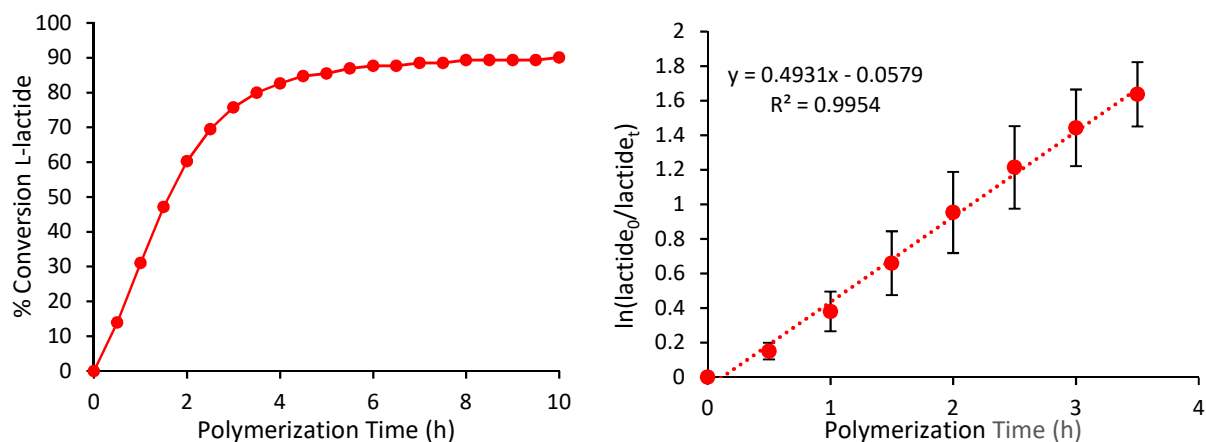


Figure A.32 Polymerization of 100 equivalents of L-LA in C_6D_6 at 90 °C using **1** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

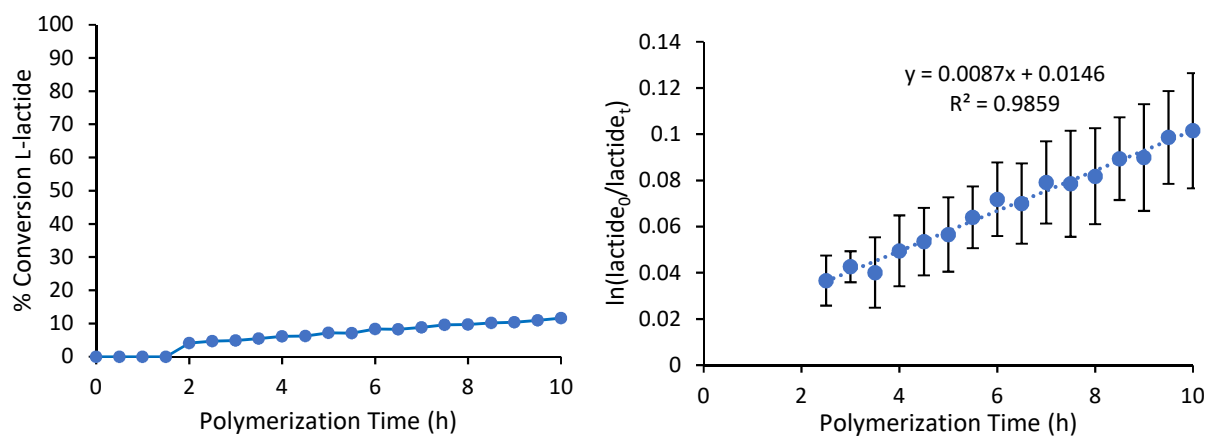


Figure A.33 Polymerization of 100 equivalents of L-LA in C_6D_6 at 90 °C using **1_{ox}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

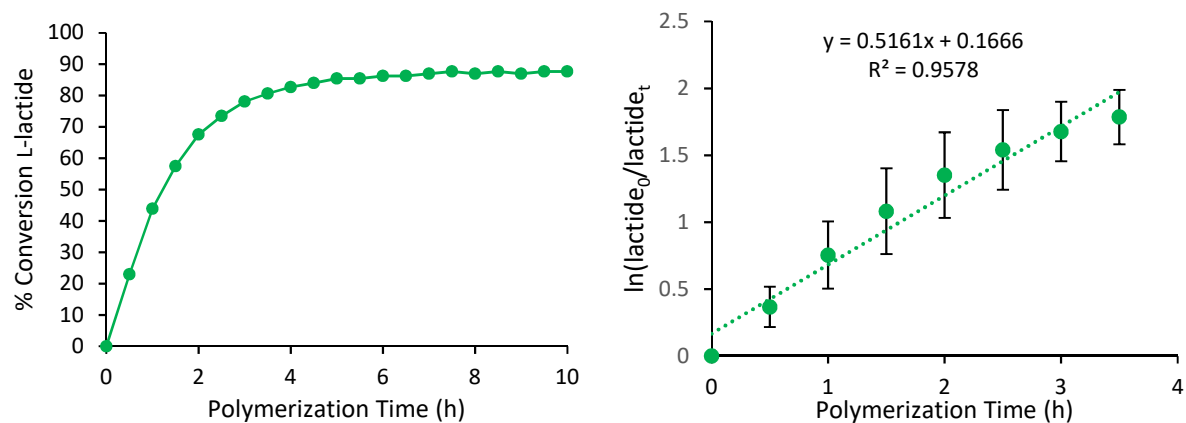


Figure A.34 Polymerization of 100 equivalents of L-LA in C_6D_6 at 90 °C using **1_{red}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

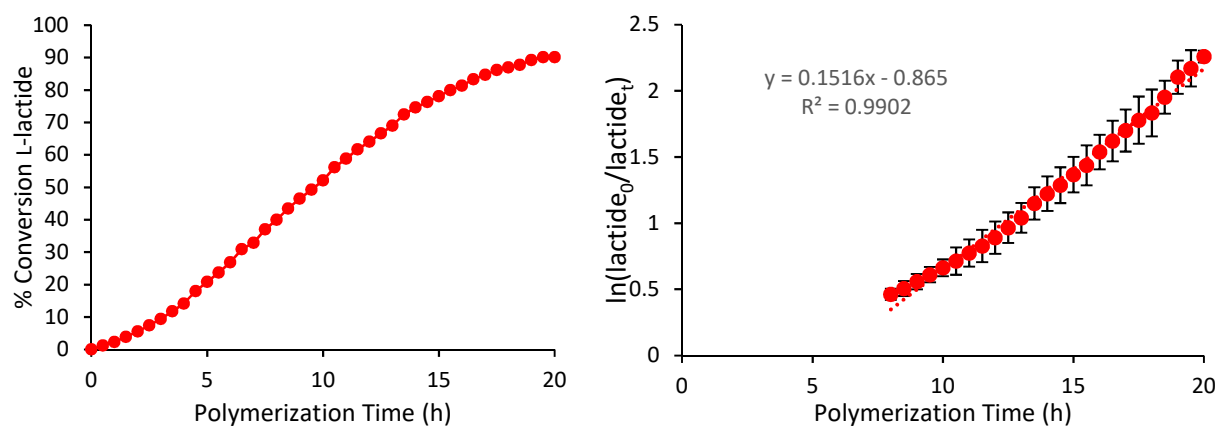


Figure A.35 Polymerization of 100 equivalents of L-LA in C_6D_6 at 90 °C using **10_{Ti}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

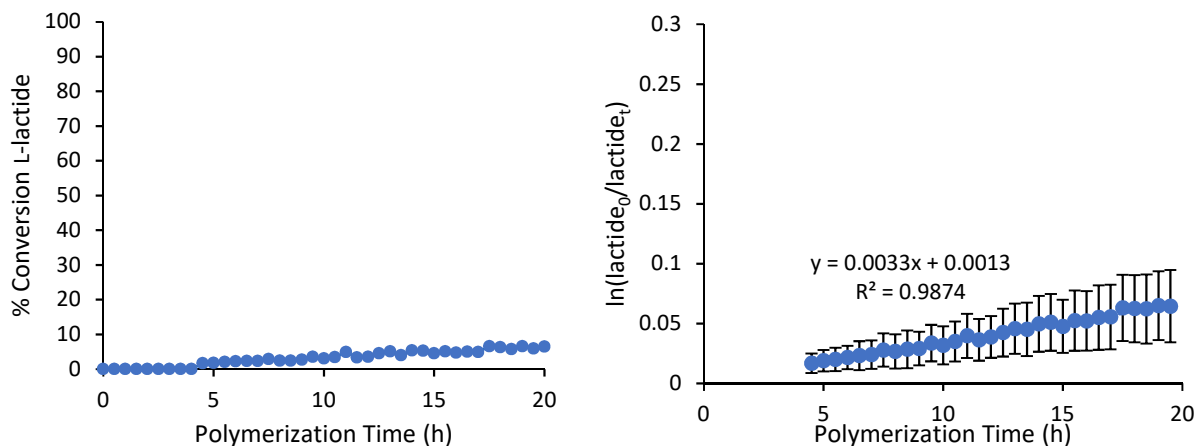


Figure A.36 Polymerization of 100 equivalents of L-LA in C_6D_6 at 90 °C using **10**_{Ti-ox} (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

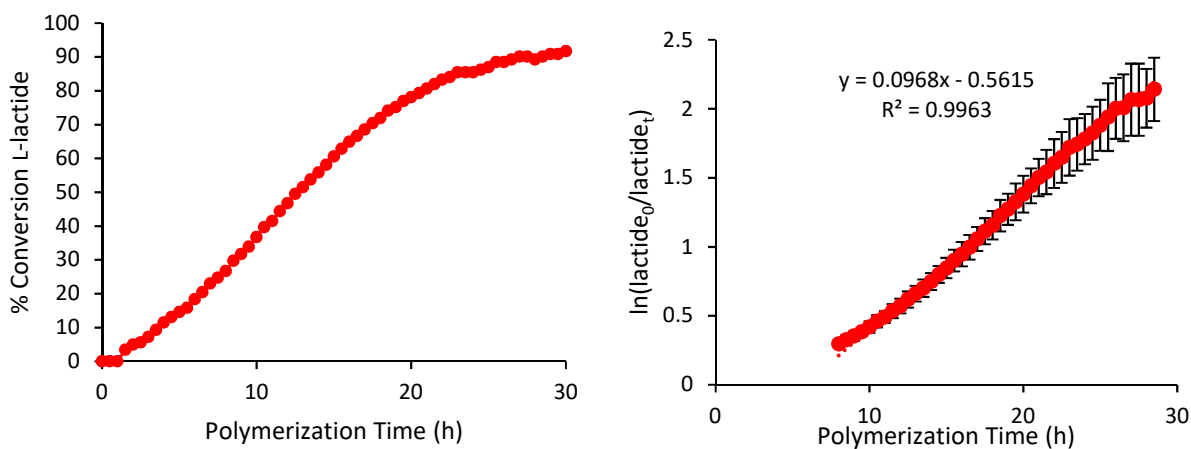


Figure A.37 Polymerization of 100 equivalents of L-LA in CDCl_3 at 90 °C using **10**_{Ti} (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

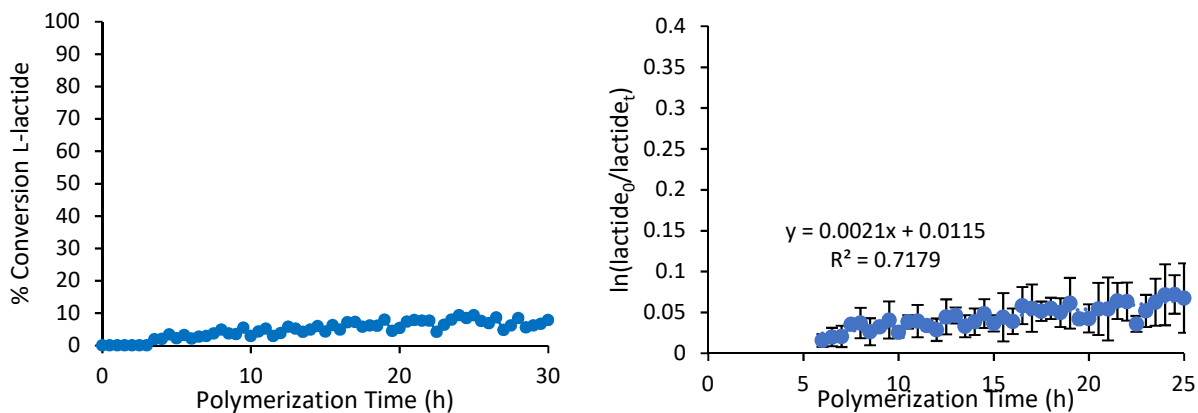


Figure A.38 Polymerization of 100 equivalents of L-LA in CDCl_3 at 90°C using **10_{Ti-ox}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

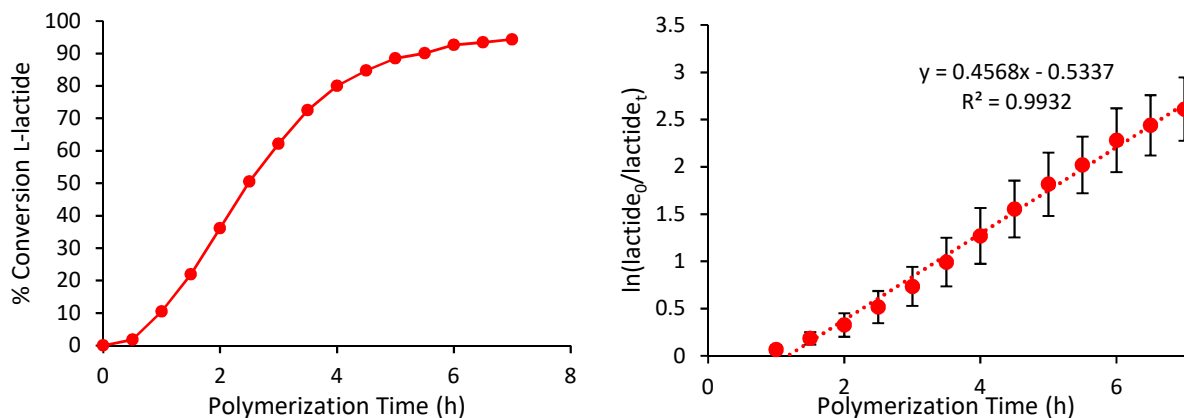


Figure A.39 Polymerization of 100 equivalents of L-LA in CDCl_3 at 90°C using **10_{Zr}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

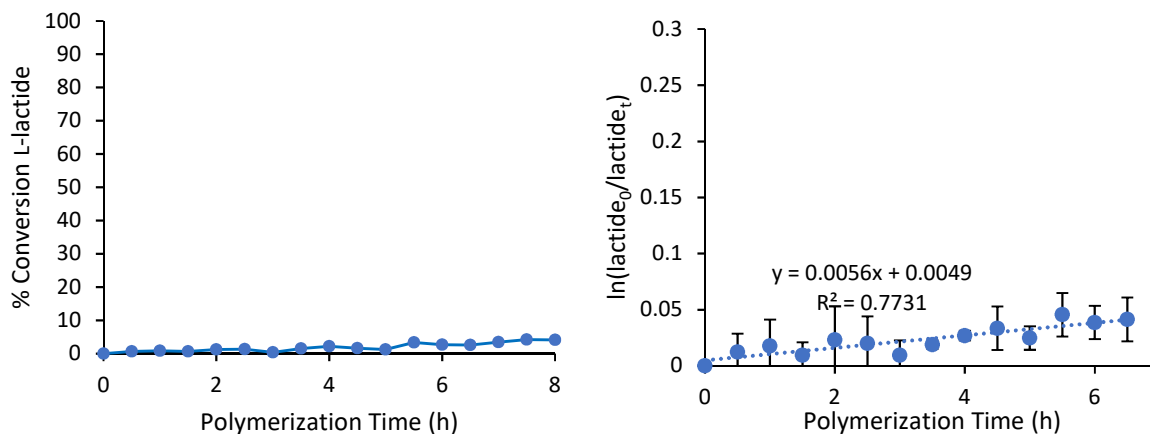


Figure A.40 Polymerization of 100 equivalents of L-LA in CDCl_3 at 90°C using **10Zr-ox** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

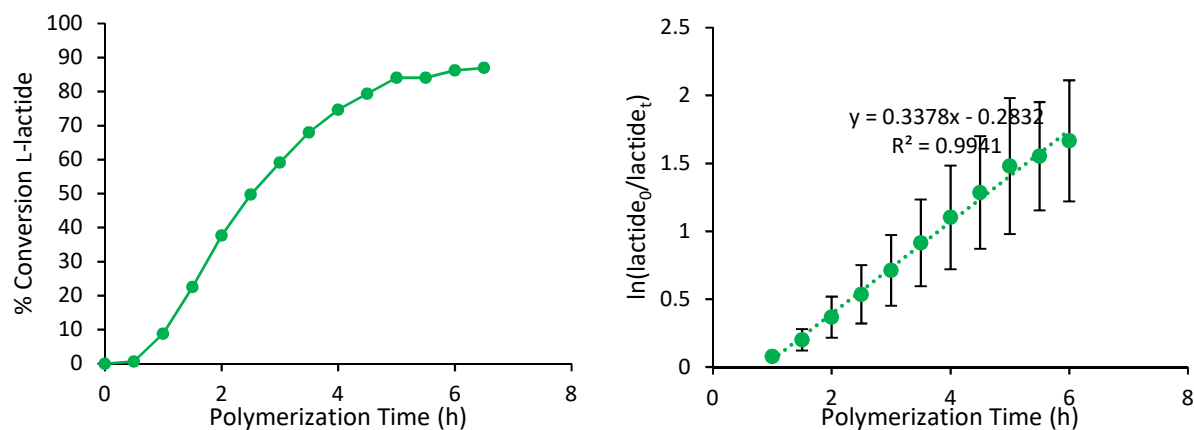


Figure A.41 Polymerization of 100 equivalents of L-LA in CDCl_3 at 90°C using **10Zr-red** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

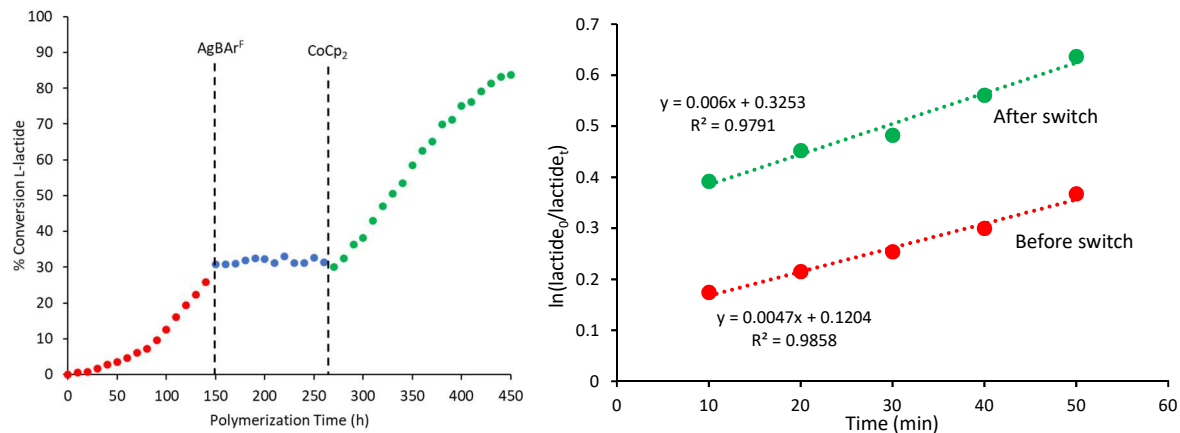


Figure A.42 In situ switching polymerization of 100 equivalents of L-LA in CDCl₃ at 90 °C starting from native catalyst **10**_{Zr} and switching at 2.5 hours and 4.5 hours (left graph), and a plot of ln(L-lactide₀/L-lactide_t) vs time (min) to study the polymerization kinetics before and after the switch (right graph).

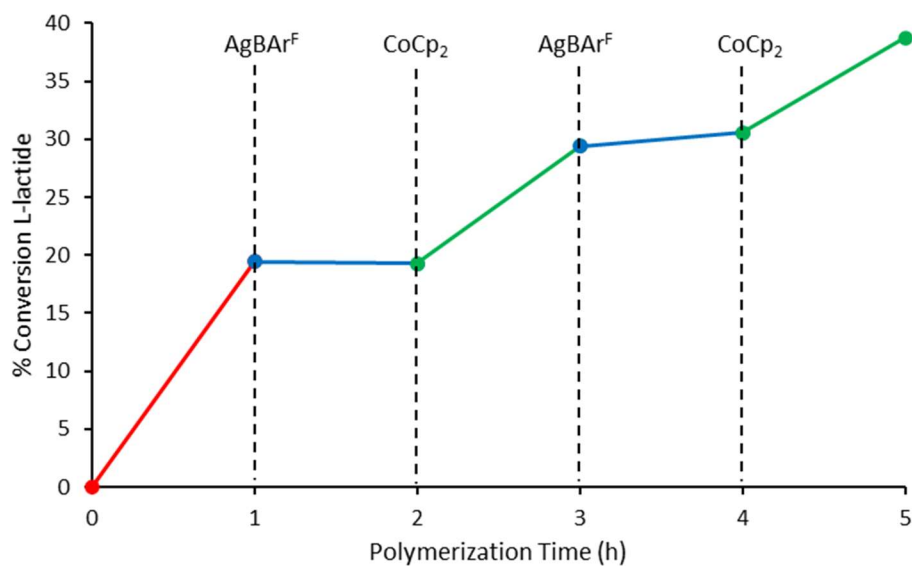


Figure A.43 In situ switching polymerization of 100 equivalents of L-LA in CDCl₃ at 90 °C starting from native catalyst **10**_{Zr} and switching to **10**_{Zr-ox} with the addition of 1 eq. AgBAR^F and **10**_{Zr-red} with the addition of 1 eq. CoCp₂ at the indicated time points.

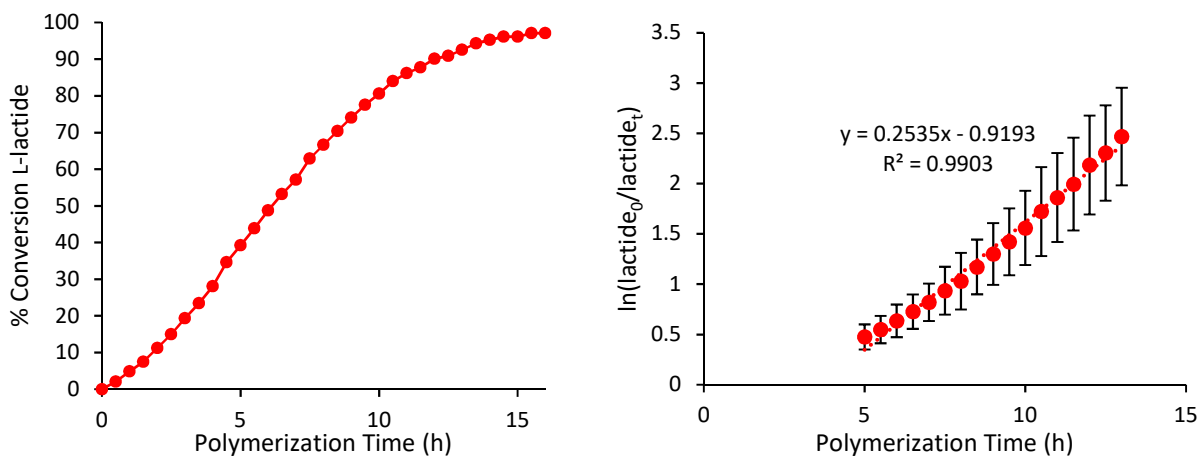


Figure A.44 Polymerization of 100 equivalents of L-LA in C_6D_6 at 90 °C using **11_{Ti}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

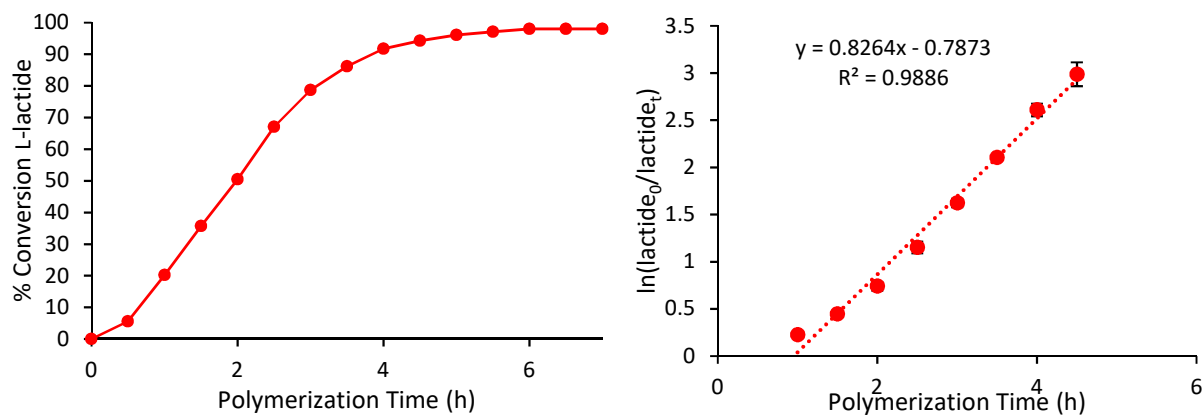


Figure A.45 Polymerization of 100 equivalents of L-LA in C_6D_6 at 90 °C using **11_{Zr}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

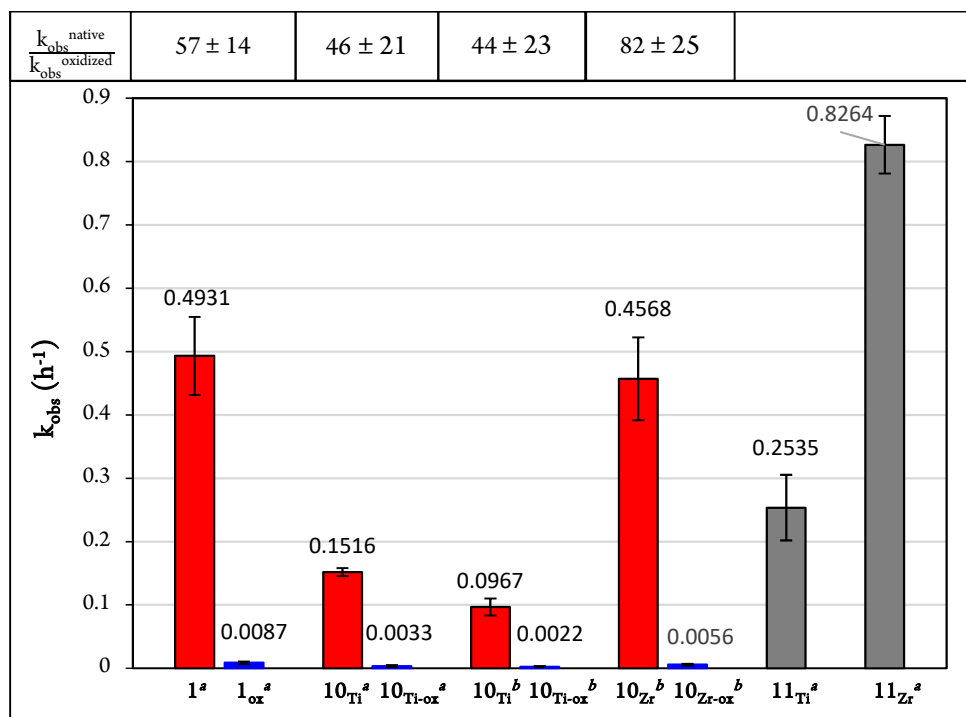


Figure A.46 Comparison of k_{obs} for each catalyst in the native state and oxidized state (when applicable). Conditions: 10 μmol catalyst, 0.7 mmol L-LA, 1 M, 90 °C. ^asolvent = C₆D₆, ^bsolvent = CDCl₃.

A.3 Experimental – Chapter 3

A.3.1 General Methods and Materials

Toluene, hexanes, and pentane were purified using a two-column purification system and degassed via freeze-pump-thaw (x3). Benzene was dried over activated molecular sieves and degassed prior to use. All NMR solvents were purchased from Cambridge Isotope Laboratories, and benzene- d_6 and chloroform- d were dried over activated molecular sieves and degassed prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 or Varian 400 MHz spectrometer. Chemical shifts are reported with respect to solvent residual peaks, 7.26 ppm (CDCl_3) or 7.16 ppm (C_6D_6). L-Lactide was purchased from Fisher Scientific and recrystallized three times from toluene prior to use. ϵ -Caprolactone was distilled off CaH_2 and degassed prior to use. Ethynyl-ferrocene,¹⁶² 3-tert-butyl-5-iodosalicylaldehyde,¹⁶³ 3-tert-butyl-5-ethynylferrocene-salicylaldehyde,⁹⁰ **L1**,⁹⁰ and **1-T**⁹⁰ were synthesized following previously reported procedures. Ethylene diamine was purified via distillation prior to use. All other reagents were purchased from commercial vendors and used without further purification. Cyclic voltammetry measurements were performed on a CH Instruments potentiostat using 0.01 mmol of the compound to be analyzed in 5 mL DCM solution (0.002 M) with supporting electrolyte 0.2 M $(\text{nBu})_4\text{NPF}_6$, using Ag/AgCl as the reference electrode, a gold working electrode, and a tungsten counter electrode at a scanning rate of 100 mV/s⁻¹. All potentials are referenced to the ferrocene/ferrocenium (Fc/Fc^+) redox couple. Molecular weights (M_n) and dispersity (Đ) of the polymers were determined using a Malvern Omisec system using triple detection and three Viscotek styrene divinylbenzene copolymer columns (in series T3000, T4000, and T5000) at a flow rate of 1 mL/min and thermostatted to 30 °C with THF as the eluent.

A.3.2 Synthesis of $(\text{C}_{48}\text{H}_{46}\text{N}_2\text{O}_2\text{Fe}_2)\text{Zr}(\text{O}^t\text{Bu})_2$ (**1_{Zr}**)

Under an inert atmosphere, $\text{Zr}(\text{O}^t\text{Bu})_4$ (0.15 mL, 0.38 mmol) was added dropwise to a toluene solution (20 mL) of **L1** (0.300 g, 0.38 mmol) and stirred overnight. The volatiles were removed under reduced pressure and the resulting orange solid was washed with either cold pentane or hexanes to yield complex **1_{Zr}**. Yield: 78% (0.307 g, 0.30 mmol). ^1H NMR (300 MHz, 25 °C, CDCl_3), δ , ppm: 1.04 (s, 9H), 1.27 (s, 9H), 1.45 (s, 18H), 3.62 (m, 2H), 3.99 (s, 1H), 4.21 (t, 4H), 4.23 (s, 10H), 4.48 (t, 4H), 7.38 (d, 2H), 7.55 (d, 2H), 8.24 (s, 2H). ^{13}C NMR (300 MHz, 25 °C, CDCl_3), δ , ppm: 29.68, 29.83, 31.40, 32.61, 32.78, 35.46, 59.93, 66.28, 68.67, 70.04, 71.35, 75.32, 85.50, 86.45, 110.24, 110.96, 122.34, 122.77, 129.27, 134.97, 136.62, 140.05, 140.55, 165.42, 166.23.

A.3.3 Synthesis of $\text{C}_{48}\text{H}_{52}\text{N}_2\text{O}_2\text{Fe}_2$ (**I12**)

To a 50:50 mixture of THF:MeOH (50 mL), was added **L1** (1.6 g, 2.00 mmol). A large excess of NaBH_4 was added slowly and the reaction was allowed to stir overnight at room temperature. All volatiles were then removed under reduced pressure followed by extraction with DCM and washing with H_2O . The organic layer was dried with sodium sulfate, decanted, and all volatiles were removed under reduced pressure to obtain the product (**I21**) as an orange solid. Yield: 84% (1.32 g, 1.68 mmol). ^1H NMR (300 MHz, 25 °C, CDCl_3), δ , ppm: 1.42 (s, 18H), 1.86 (br s, 2H), 2.84 (s, 4H), 3.98 (s, 4H), 4.22 (t, 4H), 4.25 (s, 10H), 4.48 (t, 4H), 7.04 (s, 2H), 7.35 (s, 2H). ^{13}C NMR (300 MHz, 25 °C, CDCl_3), δ , ppm: 29.40, 34.74, 47.54, 52.67, 66.11, 68.51, 69.89, 71.22, 85.49, 86.36, 113.47, 122.32, 129.72, 129.80, 137.15, 157.21.

A.3.4 Synthesis of $C_{50}H_{56}N_2O_2Fe_2$ (**L12**)

To a mixture of acetonitrile: acidic acid (17 mL:3 mL), was added **I21** (1.3 g, 1.6 mmol) and formaldehyde (1.2 mL, 16 mmol) and let stir for 1 h. All volatiles were removed under reduced pressure. The residual solid was dissolved in a 50:50 mixture of THF: MeOH (50 mL). A large excess of $NaBH_4$ was added slowly and the reaction was allowed to stir overnight at room temperature. All volatiles were then removed under reduced pressure followed by extraction with DCM and washing with H_2O . The organic layer was dried with sodium sulfate, decanted, and all volatiles were removed under reduced pressure. The crude product was then purified via silica gel plug with a 50:50 hexanes:DCM eluent to obtain **L21** as an orange solid. Yield: 58% (0.77 g, 0.92 mmol). 1H NMR (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 1.44 (s, 18H), 2.26 (s, 6H), 2.63 (s, 4H), 3.68 (s, 4H), 4.22 (t, 4H), 4.25 (s, 10H), 4.48 (t, 4H), 7.02 (s, 2H), 7.35 (s, 2H). ^{13}C NMR (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 29.77, 34.74, 41.32, 53.37, 62.11, 66.10, 68.52, 69.89, 71.22, 85.49, 86.39, 113.31, 121.95, 129.80, 129.94, 137.02, 157.08.

A.3.5 Synthesis of $(C_{50}H_{54}N_2O_2Fe_2)Ti(O^iPr)_2$ (**12_{Ti}**)

Under an inert atmosphere, $Ti(O^iPr)_4$ (0.09 mL, 0.30 mmol) was added dropwise to a toluene solution (10 mL) of **L21** (0.250 g, 0.30 mmol) and stirred overnight. The volatiles were removed under reduced pressure and the resulting orange solid was washed with either cold pentane or hexanes to yield complex **21_{Ti}**. Yield: 60% (0.1775 g, 0.179 mmol). 1H NMR (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 1.09 (d, 6H), 1.21 (d, 6H), 1.51 (s, 18H), 1.87 (d, 2H), 2.46 (s, 6H), 3.14 (m, 4H), 4.29-4.24 (t, 4H and s, 10H), 4.41 (d, 2H), 4.46 (t, 4H), 4.82 (m, 2H), 7.03 (s, 2H), 7.37 (s, 2H). ^{13}C NMR (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 26.19, 26.53, 30.06, 35.00, 48.53, 52.39, 64.71, 66.52, 68.39, 69.86, 71.16, 78.22, 85.17, 87.00, 110.90, 123.91, 130.08, 130.96, 137.39, 162.02.

A.3.6 Synthesis of $(C_{50}H_{54}N_2O_2Fe_2)Zr(O^iBu)_2$ (**12_{Zr}**)

Under an inert atmosphere, $Zr(O^iBu)_4$ (0.12 mL, 0.30 mmol) was added dropwise to a toluene solution (15 mL) of **L21** (0.25 g, 0.30 mmol) and stirred overnight. The volatiles were removed under reduced pressure and the resulting orange solid was washed with either cold pentane or hexanes to yield complex **21_{Zr}**. Yield: 70% (0.22 g, 0.23 mmol). 1H NMR (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 1.28 (s, 18H), 1.50 (s, 18H), 1.82 (d, 2H), 2.45 (s, 6H), 3.12 (dd, 4H), 4.20 (t, 4H), 4.23 (s, 10H), 4.46 (t, 4H), 4.62 (d, 2H), 7.04 (s, 2H), 7.39 (s, 2H). ^{13}C NMR (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 29.83, 33.07, 35.07, 51.64, 64.38, 64.45, 66.51, 68.39, 69.86, 71.15, 76.63, 84.78, 86.90, 110.73, 123.99, 130.49, 131.42, 138.21, 160.94.

A.3.7 General Procedure for NMR Scale Polymerization of L-lactide

In a glove box, L-lactide (0.7 mmol), catalyst (0.007 mmol), trimethoxybenzene (internal standard) (0.035 mmol), and benzene- d_6 (0.7 mL) were added to a J. Young NMR tube equipped with a Teflon valve. The NMR tube was removed from the glove box, and the polymerization was monitored by 1H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad”, respectively, were used collected data every 2, 5, or 10 minutes and the data was processed with VnmrJ 4.2, respectively. Conversion of L-lactide was monitored by comparing the methine peak of the monomer to the methine peak of the polymer.

A.3.8 NMR Scale Polymerization of L-lactide using **1**_{Ti-ox} and **1**_{Zr-ox}

In a glove box, catalyst (0.007 mmol) was added to a vial with benzene-*d*₆ (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve containing AgOTf (0.014 mmol), shaken well, and heated at 90 °C for 30 minutes. After cooling to room temperature L-lactide (0.7 mmol) and trimethoxybenzene (internal standard) (0.035 mmol) were added to the J. Young NMR tube. The NMR tube was removed from the glove box, and the polymerization was monitored by ¹H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad” was used to collect data every 2, 5, or 10 minutes and the data was processed with VnmrJ 4.2. Conversion of L-lactide was monitored by comparing the methine peak of the monomer to the methine peak of the polymer.

A.3.9 NMR Scale Polymerization of L-lactide using **12**_{Ti-ox} and **12**_{Zr-ox}

In a glove box, catalyst (0.007 mmol) was added to a vial with benzene-*d*₆ (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve containing AgOTf (0.014 mmol), L-lactide (0.7 mmol), and trimethoxybenzene (internal standard) (0.035 mmol). The NMR tube was shaken well, removed from the glove box, and the polymerization was monitored by ¹H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad” was used to collect data every 2, 5, or 10 minutes and the data was processed with VnmrJ 4.2. Conversion of L-lactide was monitored by comparing the methine peak of the monomer to the methine peak of the polymer.

A.3.10 NMR Scale Polymerization of L-lactide using **1**_{Ti-red} and **1**_{Zr-red}

In a glove box, catalyst (0.007 mmol) was added to a vial with benzene-*d*₆ (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve containing AgOTf (0.014 mmol), shaken well, and heated at 90 °C for 30 minutes. After cooling to room temperature CoCp₂ (0.014 mmol), L-lactide (0.7 mmol) and trimethoxybenzene (internal standard) (0.035 mmol) were added to the J. Young NMR tube. The NMR tube was removed from the glove box, and the polymerization was monitored by ¹H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad” was used to collect data every 2, 5, or 10 minutes and the data was processed with VnmrJ 4.2. Conversion of L-lactide was monitored by comparing the methine peak of the monomer to the methine peak of the polymer.

A.3.11 NMR Scale Polymerization of L-lactide using **12**_{Ti-red} and **12**_{Zr-red}

In a glove box, catalyst (0.007 mmol) was added to a vial with benzene-*d*₆ (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve containing AgOTf (0.014 mmol), L-lactide (0.7 mmol), and trimethoxybenzene (internal standard) (0.035 mmol). The NMR tube was shaken well then CoCp₂ (0.014 mmol) was added to the J. Young tube and shaken well. The J. Young tube removed from the glove box and the polymerization was monitored by ¹H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad” was used to collect data every 2, 5, or 10 minutes and the data was processed with VnmrJ 4.2. Conversion of L-lactide was monitored by comparing the methine peak of the monomer to the methine peak of the polymer.

A.3.12 General Procedure for NMR Scale Polymerization of ϵ -Caprolactone

In a glove box, ϵ -caprolactone (0.7 mmol), catalyst (0.007 mmol), trimethoxybenzene (internal standard) (0.035 mmol), and benzene- d_6 (0.7 mL) were added to a J. Young NMR tube equipped with a Teflon valve. The NMR tube was removed from the glove box, and the polymerization was monitored by ^1H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad”, respectively, were used collected data every 10 minutes and the data was processed with VnmrJ 4.2, respectively. Conversion of ϵ -caprolactone was monitored by comparing the methylene peak of the monomer to the methylene peak of the polymer.

A.3.13 NMR Scale Polymerization of ϵ -Caprolactone using **1**_{Ti-ox} and **1**_{Zr-ox}

In a glove box, catalyst (0.007 mmol) was added to a vial with benzene- d_6 (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve containing AgOTf (0.014 mmol), shaken well, and heated at 90 °C for 30 minutes. After cooling to room temperature ϵ -Caprolactone (0.7 mmol) and trimethoxybenzene (internal standard) (0.035 mmol) were added to the J. Young NMR tube. The NMR tube was removed from the glove box, and the polymerization was monitored by ^1H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad” was used to collect data every 10 minutes and the data was processed with VnmrJ 4.2. Conversion of ϵ -Caprolactone was monitored by comparing the methylene peak of the monomer to the methylene peak of the polymer.

A.3.14 NMR Scale Polymerization of ϵ -Caprolactone using **12**_{Ti-ox} and **12**_{Zr-ox}

In a glove box, catalyst (0.007 mmol) was added to a vial with benzene- d_6 (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve containing AgOTf (0.014 mmol), ϵ -Caprolactone (0.7 mmol), and trimethoxybenzene (internal standard) (0.035 mmol). The NMR tube was shaken well, removed from the glove box, and the polymerization was monitored by ^1H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad” was used to collect data every 10 minutes and the data was processed with VnmrJ 4.2. Conversion of ϵ -Caprolactone was monitored by comparing the methylene peak of the monomer to the methylene peak of the polymer.

A.3.15 NMR Scale Polymerization of ϵ -Caprolactone using **1**_{Ti-red} and **1**_{Zr-red}

In a glove box, catalyst (0.007 mmol) was added to a vial with benzene- d_6 (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve containing AgOTf (0.014 mmol), shaken well, and heated at 90 °C for 30 minutes. After cooling to room temperature CoCp₂ (0.014 mmol), ϵ -Caprolactone (0.7 mmol) and trimethoxybenzene (internal standard) (0.035 mmol) were added to the J. Young NMR tube. The NMR tube was removed from the glove box, and the polymerization was monitored by ^1H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad” was used to collect data every 10 minutes and the data was processed with VnmrJ 4.2. Conversion of ϵ -Caprolactone was monitored by comparing the methylene peak of the monomer to the methylene peak of the polymer.

A.3.16 NMR Scale Polymerization of ϵ -Caprolactone using **12**_{Ti-red} and **12**_{Zr-red}

In a glove box, catalyst (0.007 mmol) was added to a vial with benzene- d_6 (0.7 mL). The solution was added to a J. Young NMR tube equipped with a Teflon valve containing AgOTf (0.014 mmol), ϵ -Caprolactone (0.7

mmol), and trimethoxybenzene (internal standard) (0.035 mmol). The NMR tube was shaken well then CoCp_2 (0.014 mmol) was added to the J. Young tube and shaken well. The J. Young tube removed from the glove box and the polymerization was monitored by ^1H NMR spectroscopy by placing the sample in a Varian 400 MHz NMR at 90 °C. The array “pad” was used to collect data every 10 minutes and the data was processed with VnmrJ 4.2. Conversion of ϵ -Caprolactone was monitored by comparing the methylene peak of the monomer to the methylene peak of the polymer.

A.3.17 General Polymerization Procedure

In a glove box, monomer (1.0 mmol), catalyst (0.01 mmol), and C_6H_6 (1.0 mL) were added to a vial. The mixture was heated with stirring at 90 °C. Polymerization was continued for a prescribed time interval before being cooled and quenched via exposure of the reaction mixture to air. The solvent was removed in vacuo and the remaining solid was dissolved in dichloromethane and precipitated into methanol to yield PLA or PCL as a white solid, which was dried under reduced pressure.

A.4 Supporting Information – Chapter 3

A.4.1 NMR Spectroscopy

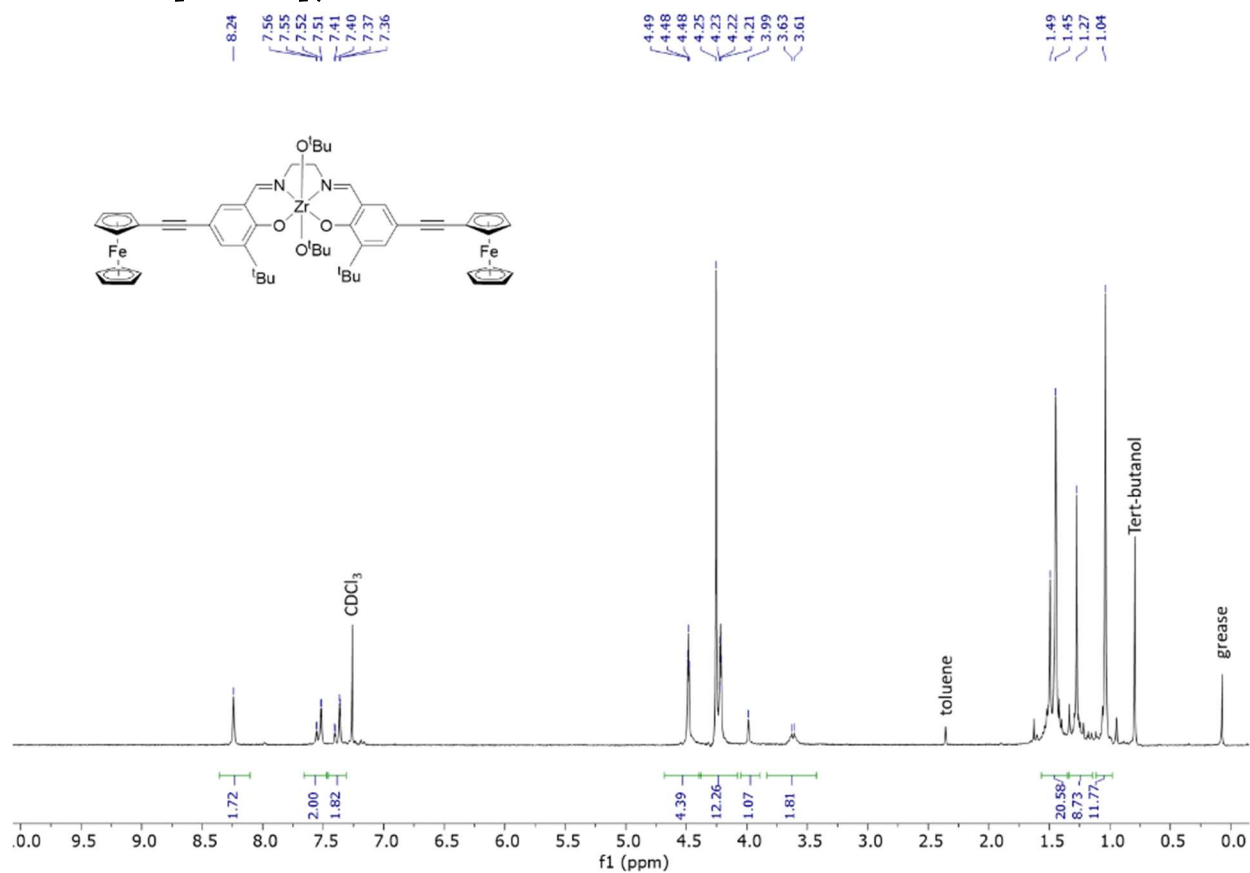


Figure A.47 ¹H NMR (300 MHz, 25 °C, CDCl₃) of **1z** δ, ppm: 1.04 (s, 9H, CCH₃), 1.27 (s, 9H, CCH₃), 1.45 (s, 18H, CCH₃), 3.62 (m, 2H, CH₂), 3.99 (s, 1H, CH₂) 4.21 (t, 4H, Cp), 4.23 (s, 10H, Cp), 4.48 (t, 4H, Cp), 7.38 (d, 2H, aromatic), 7.55 (d, 2H, aromatic), 8.24 (s, 2H, HC=N).

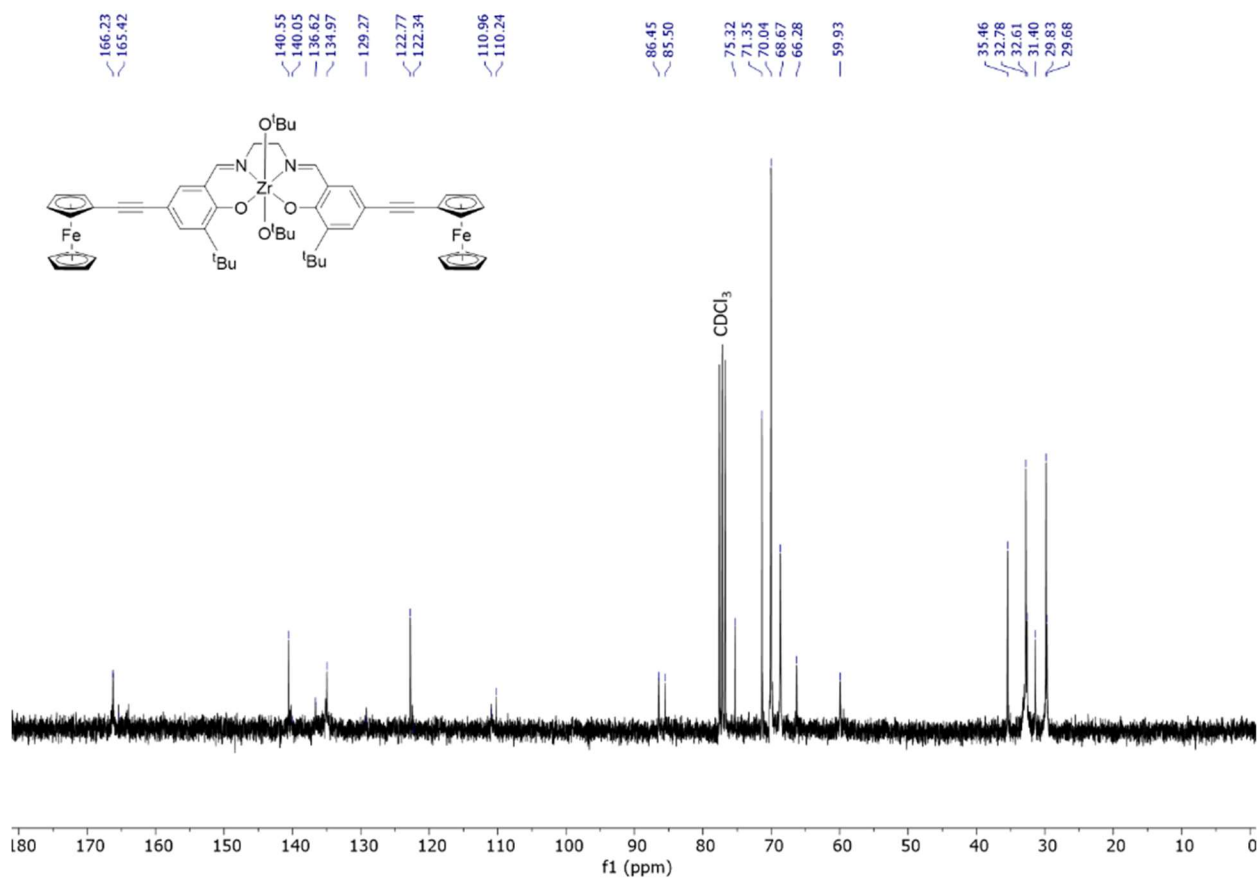


Figure A.48 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of **1_{Zr}** δ, ppm: 29.68 (CH₃), 29.83 (CH₃), 31.40 (CH₃), 32.61 (CH₃), 32.78 (CH₃), 35.46 (CCH₃), 59.93 (NCH₂), 66.28 (Cp-C), 68.67 (Cp-C), 70.04 (Cp-C), 71.35 (Cp-C), 75.32 (CCH₃), 85.50 (C≡C), 86.45 (C≡C), 110.24 (aromatic), 110.96 (aromatic), 122.34 (aromatic), 122.77 (aromatic), 129.27 (aromatic), 134.97 (aromatic), 136.62 (aromatic), 140.05 (aromatic), 140.55 (aromatic), 165.42 (C=N), 166.23 (C=N).

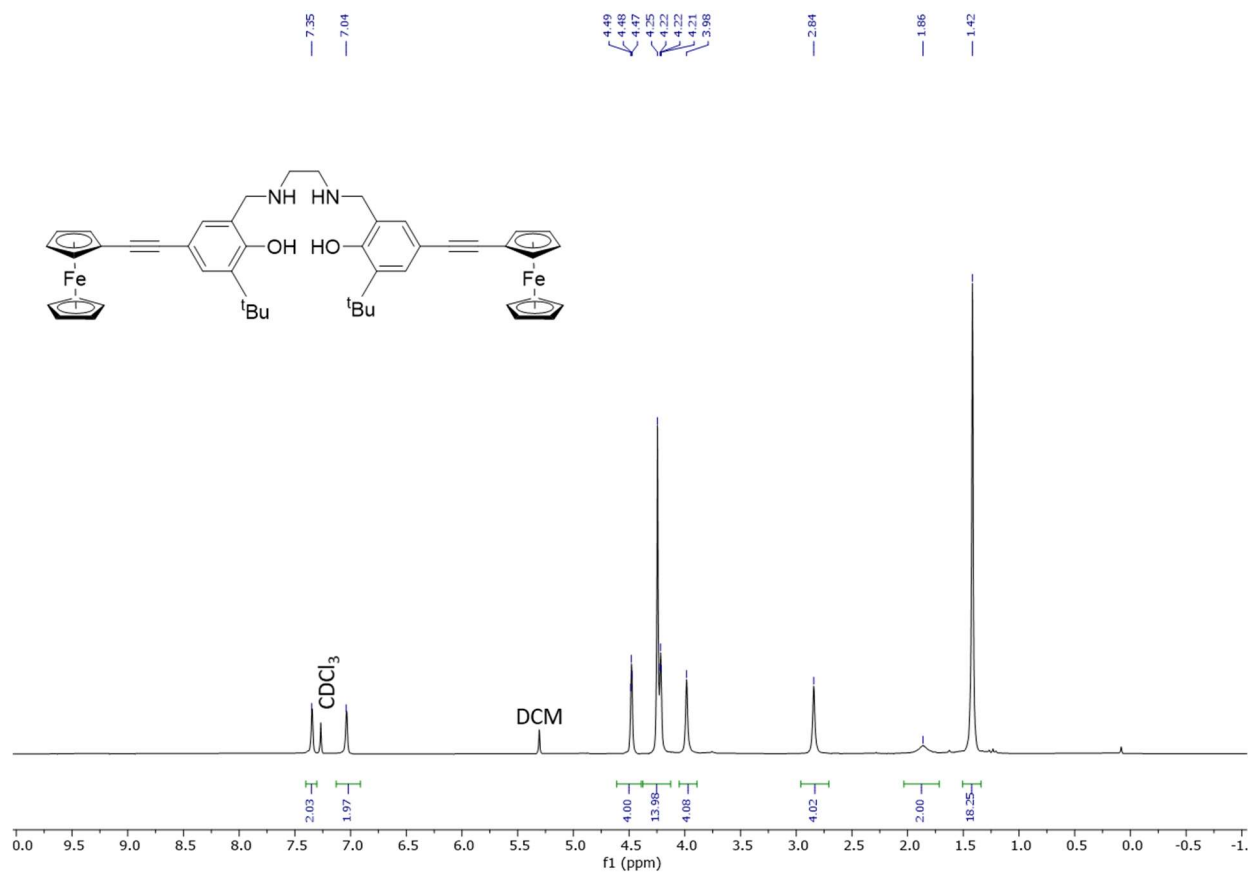


Figure A.49 ^1H NMR (300 MHz, 25 °C, CDCl_3) of **112**, δ , ppm: 1.42 (s, 18H, CH_3), 1.86 (br s, 2H, NH), 2.84 (s, 4H, NCH_2), 3.98 (s, 4H, NCH_2), 4.22 (t, 4H, CpH), 4.25 (s, 10H, CpH), 4.48 (t, 4H, CpH), 7.04 (s, 2H, PhH), 7.35 (s, 2H, PhH).

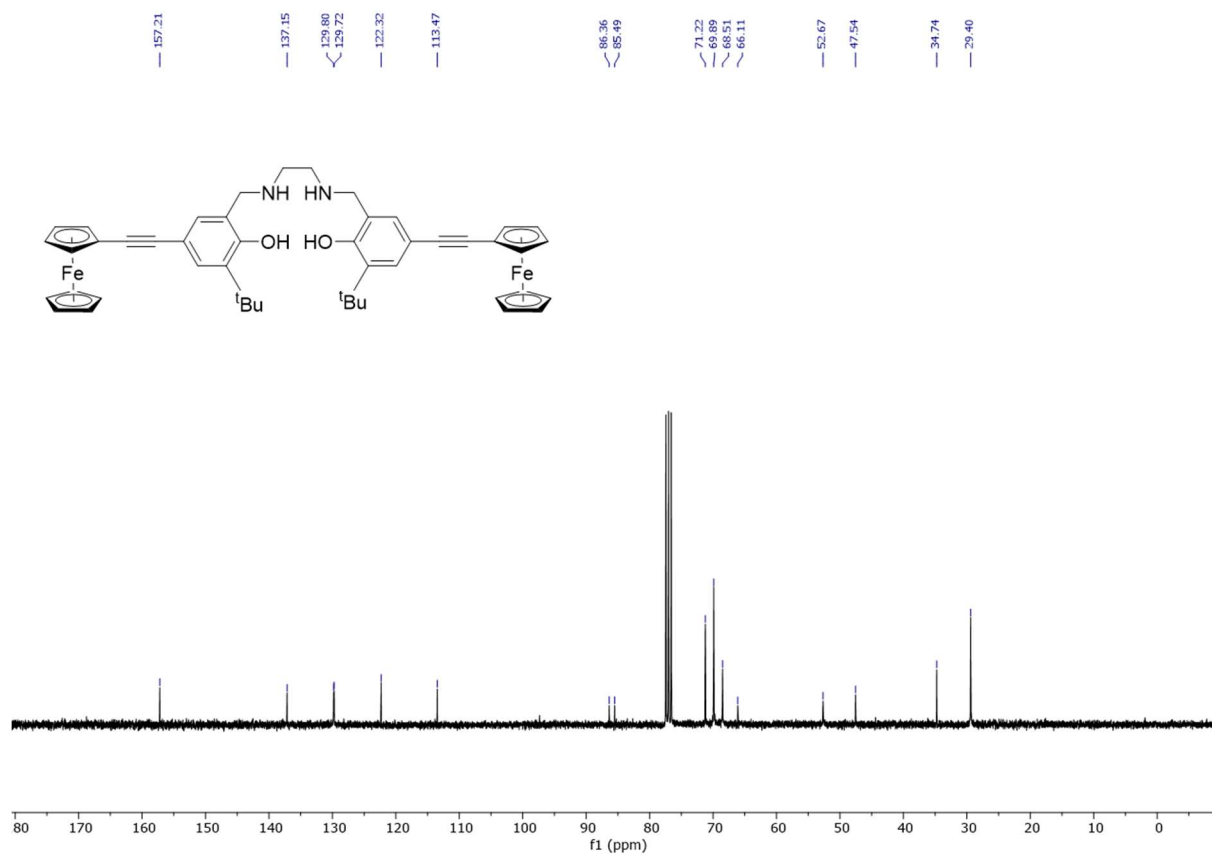


Figure A.50 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of **112**, δ , ppm: 29.40 ($\text{C}(\text{CH}_3)_3$), 34.74 ($\text{C}(\text{CH}_3)_3$), 47.54 (NCH_2), 52.67 (NCH_2), 66.11 (Cp-C), 68.51 (Cp-C), 69.89 (Cp-C), 71.22 (Cp-C), 85.49 ($\text{C}\equiv\text{C}$), 86.36 ($\text{C}\equiv\text{C}$), 113.47 (aromatic), 122.32 (aromatic), 129.72 (aromatic), 129.80 (aromatic), 137.15 (aromatic), 157.21 (aromatic).

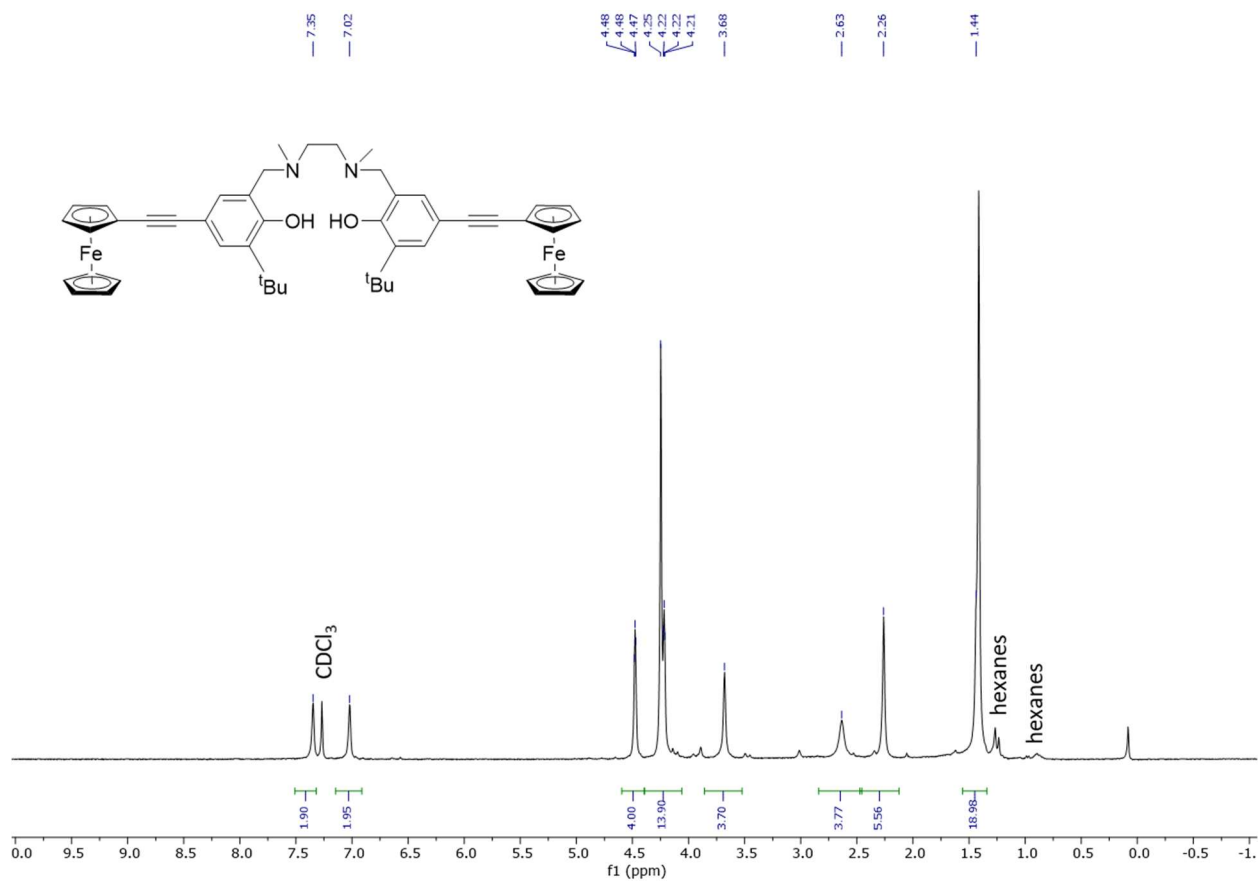


Figure A.S1 ^1H NMR (300 MHz, 25°C , CDCl_3) of **L12**, δ , ppm: 1.44 (s, 18H, CH₃), 2.26 (s, 6H, NCH₃), 2.63 (s, 4H, NCH₂), 3.68 (s, 4H, NCH₂), 4.22 (t, 4H, Cp-H), 4.25 (s, 10H, Cp-H), 4.48 (t, 4H, Cp-H), 7.02 (s, 2H, PhH), 7.35 (s, 2H, PhH).

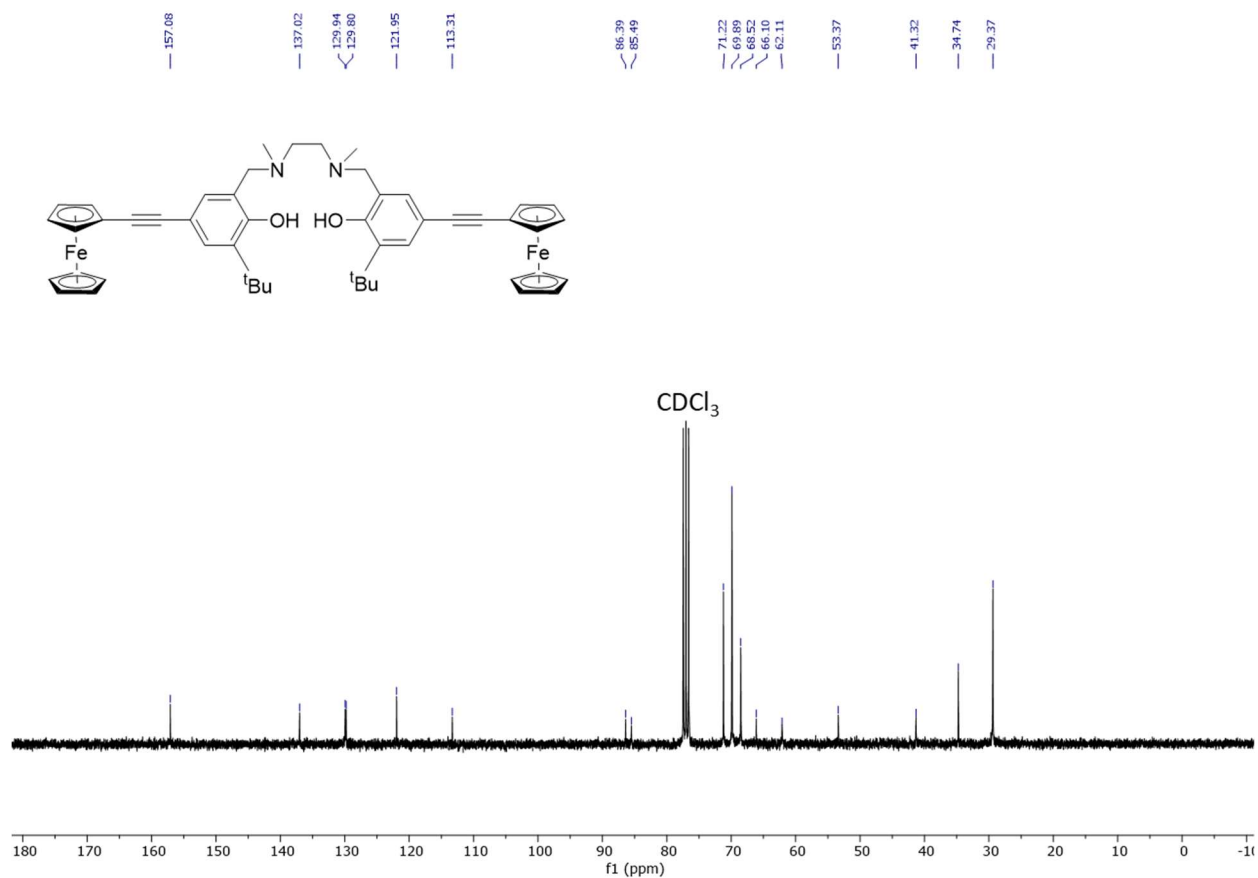


Figure A.52 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of **L12**, δ , ppm: 29.77 ($\text{C}(\text{CH}_3)_3$), 34.74 ($\text{C}(\text{CH}_3)_3$), 41.32 (NCH_3), 53.37 (NCH_2), 62.11 (NCH_2), 66.10 (Cp-C), 68.52 (Cp-C), 69.89 (Cp-C), 71.22 (Cp-C), 85.49 ($\text{C}\equiv\text{C}$), 86.39 ($\text{C}\equiv\text{C}$), 113.31 (aromatic), 121.95 (aromatic), 129.80 (aromatic), 129.94 (aromatic), 137.02 (aromatic), 157.08 (aromatic).

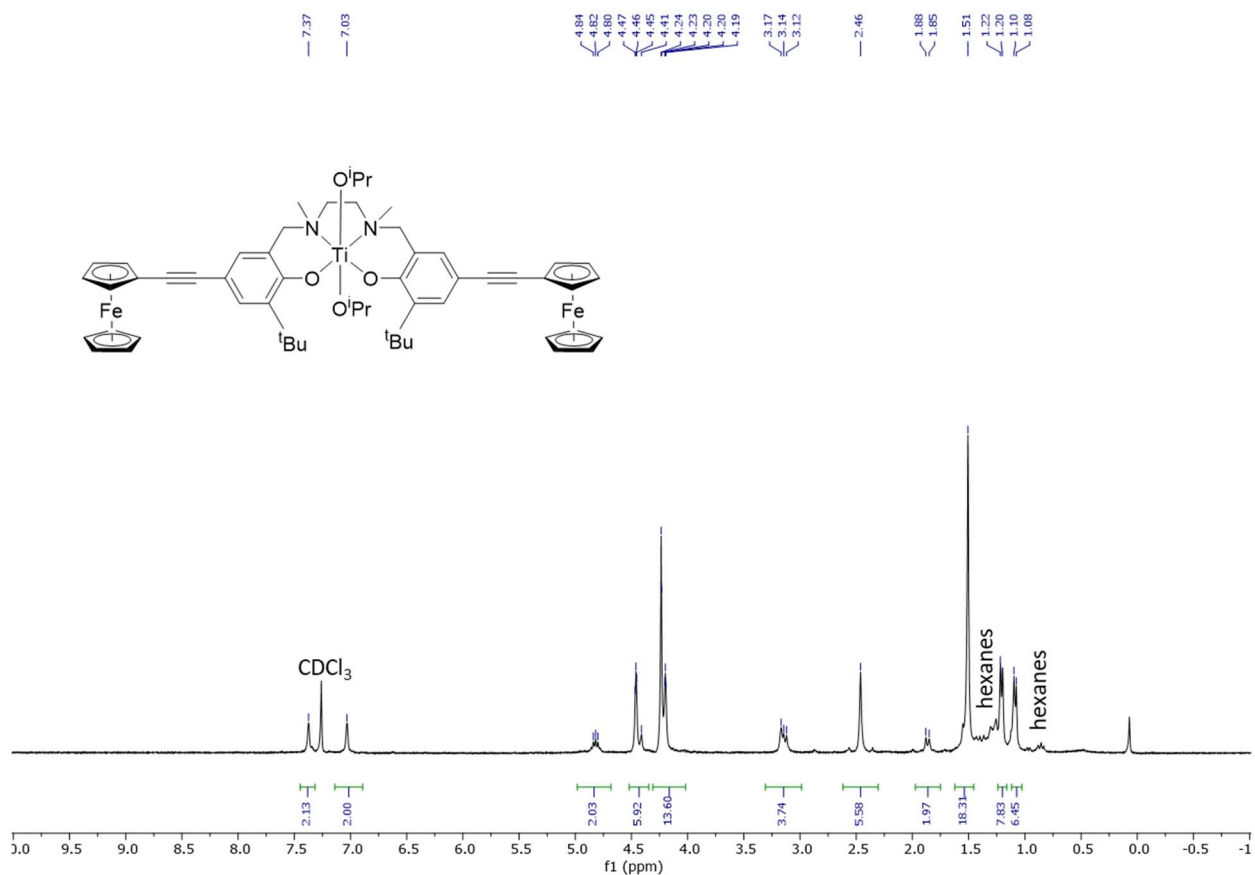


Figure A.53 ¹H NMR (300 MHz, 25 °C, CDCl₃) of **12_{Ti} δ**, ppm: 1.09 (d, 6H, CH₃), 1.21 (d, 6H, CH₃), 1.51 (s, 18H, CH₃), 1.87 (d, 2H, NCH₂), 2.46 (s, 6H, NCH₃), 3.14 (m, 4H, NCH₂), 4.29-4.24 (t, 4H, CpH and s, 10H, CpH), 4.41 (d, 2H, NCH₂), 4.46 (t, 4H, CpH), 4.82 (m, 2H, OCH), 7.03 (s, 2H, PhH), 7.37 (s, 2H, PhH).

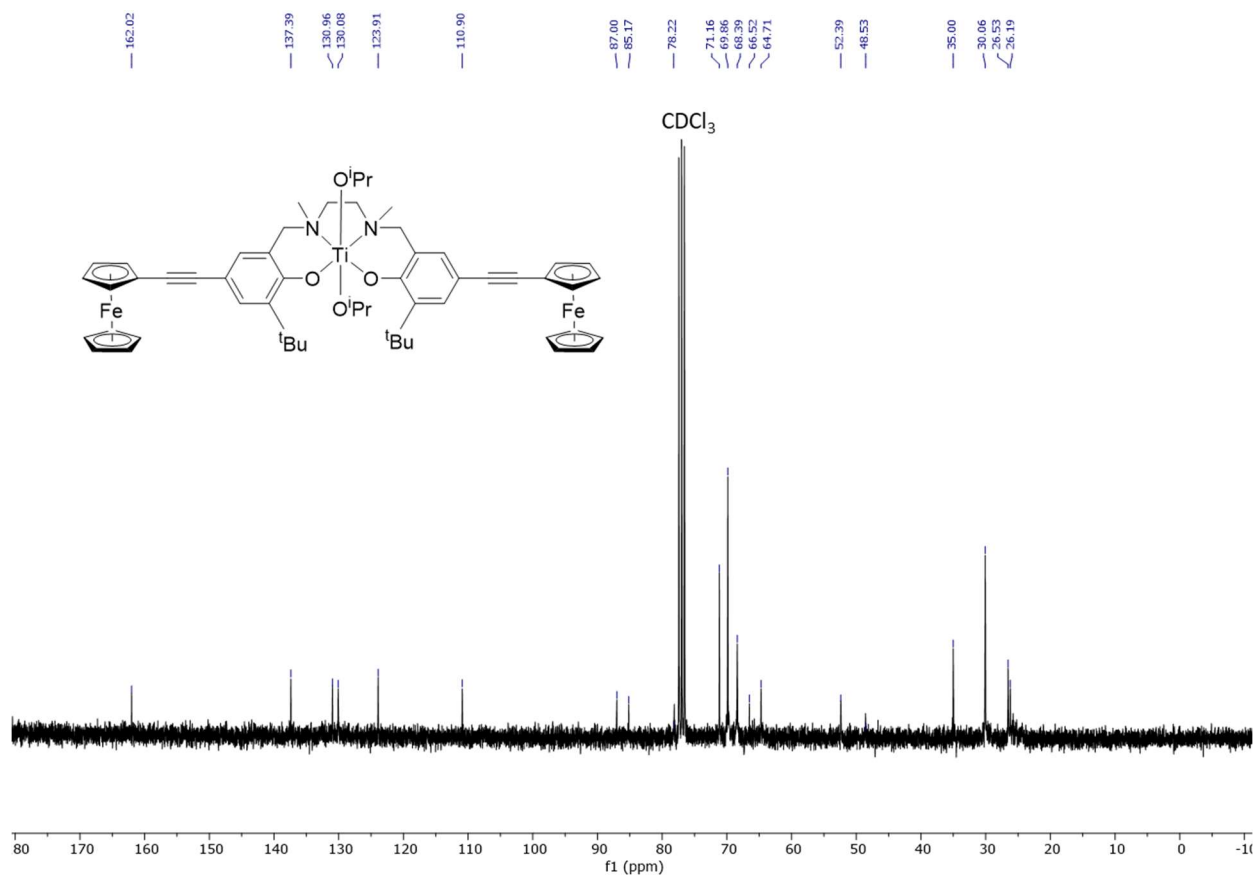


Figure A.54 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of **12_{Ti}** δ, ppm: 26.19 (CH(CH₃)₂), 26.53 (CH(CH₃)₂), 30.06 (C(CH₃)₃), 35.00 (C(CH₃)₃), 48.53 NCH₂, 52.39 (NCH₃), 64.71 (NCH₂), 66.52 (Cp-C), 68.39 (Cp-C), 69.86 (Cp-C), 71.16 (Cp-C), 78.22 (CH(CH₃)₂), 85.17 (C≡C), 87.00 (C≡C), 110.90 (aromatic), 123.91 (aromatic), 130.08 (aromatic), 130.96 (aromatic), 137.39 (aromatic), 162.02 (aromatic).

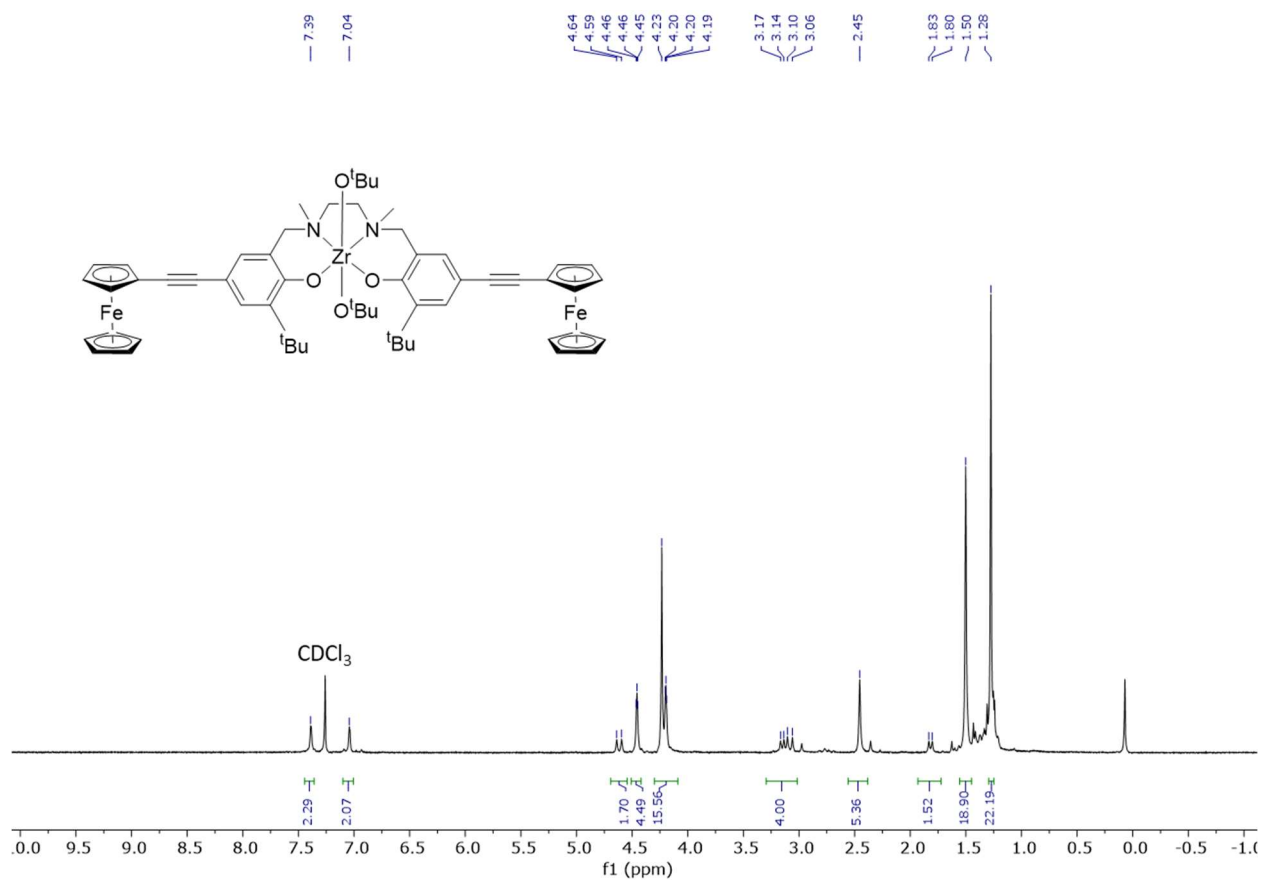


Figure A.55 ¹H NMR (300 MHz, 25 °C, CDCl₃) of **12_{zr}** δ, ppm: 1.28 (s, 18H, CCH₃), 1.50 (s, 18H, CCH₃), 1.82 (d, 2H, CH₂), 2.45 (s, 6H, CH₃), 3.12 (dd, 4H, CH₂), 4.20 (t, 4H, Cp), 4.23 (s, 10H, Cp), 4.46 (t, 4H, Cp), 4.62 (d, 2H, CH₂), 7.04 (s, 2H, aromatic), 7.39 (s, 2H, aromatic).

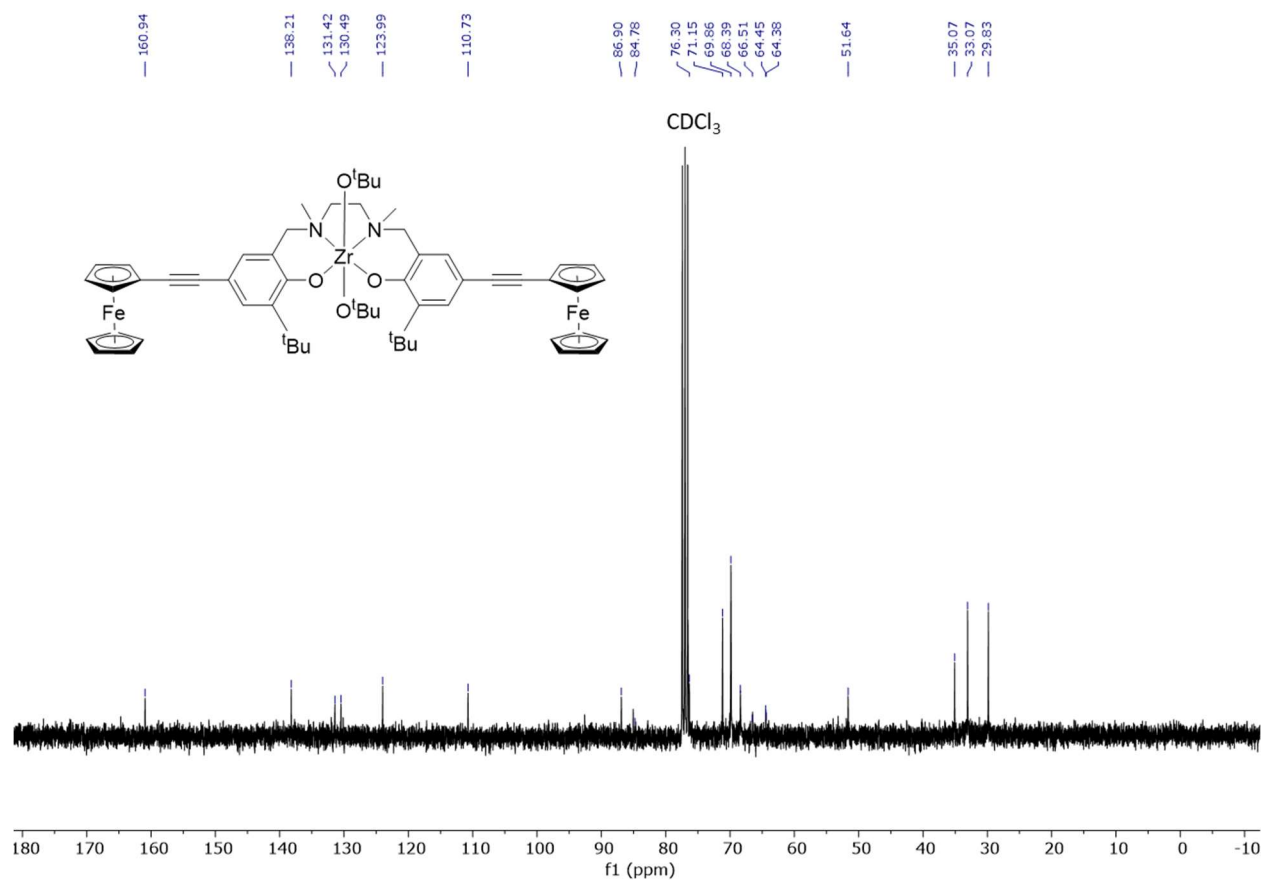


Figure A.56 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of **12_{zx}** δ, ppm: 29.83 (CCH₃), 33.07 (CH₃), 35.07 (CH₃), 51.64 (NCH₃), 64.38 (CH₂), 64.45 (CH₂), 66.51 (Cp-C), 68.39 (Cp-C), 69.86 (Cp-C), 71.15 (Cp-C), 76.30 (CCH₃), 84.78 (C≡C), 86.90 (C≡C), 110.73 (aromatic), 123.99 (aromatic), 130.49 (aromatic), 131.42 (aromatic), 138.21 (aromatic), 160.94 (aromatic).

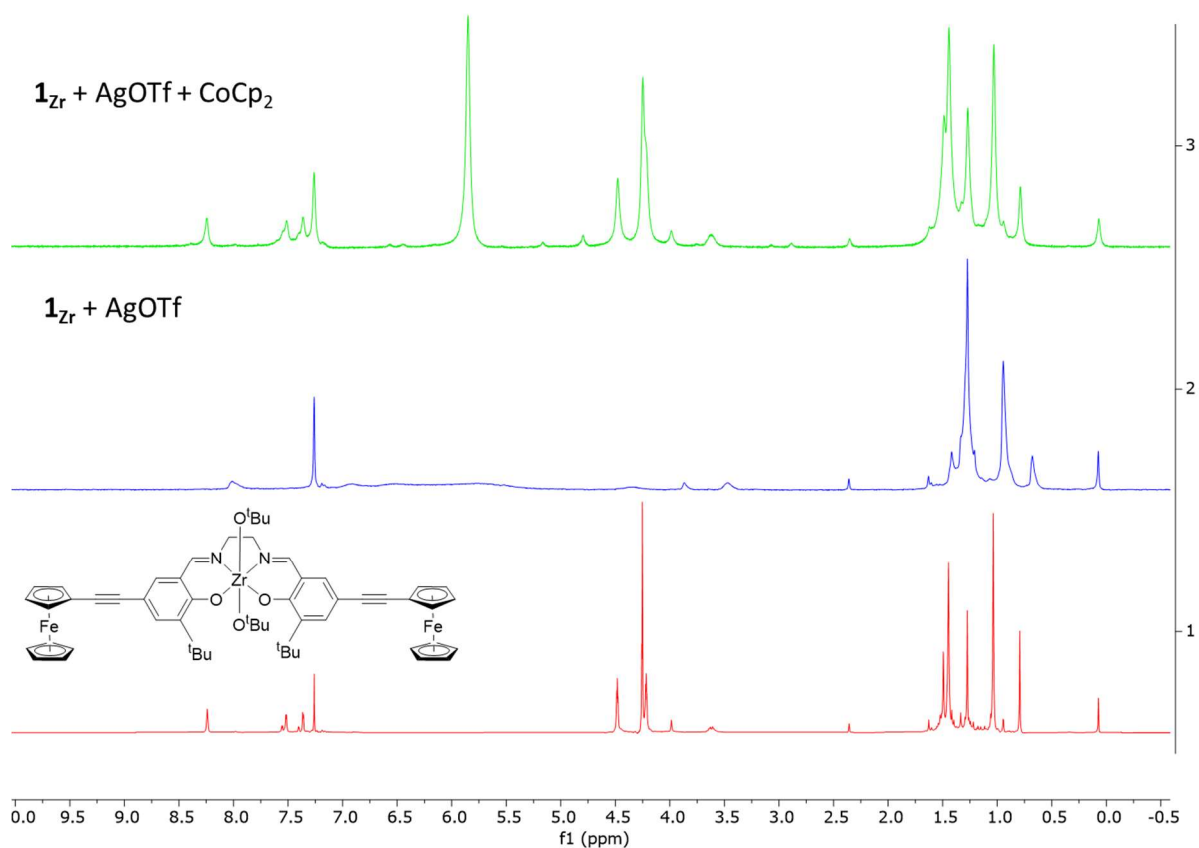


Figure A.57 ^1H NMR (300 MHz, 25 $^\circ\text{C}$, CDCl_3) of 1_{Zr} (bottom), $1_{\text{Zr-ox}}$ (middle), and $1_{\text{Zr-red}}$ (top). $1_{\text{Zr-ox}}$ was generated by the addition of 2 equivalence of AgOTf to **1** in CDCl_3 in a J. Young NMR tube. $1_{\text{Zr-red}}$ was generated by the subsequent addition of CoCp_2 to the NMR tube.

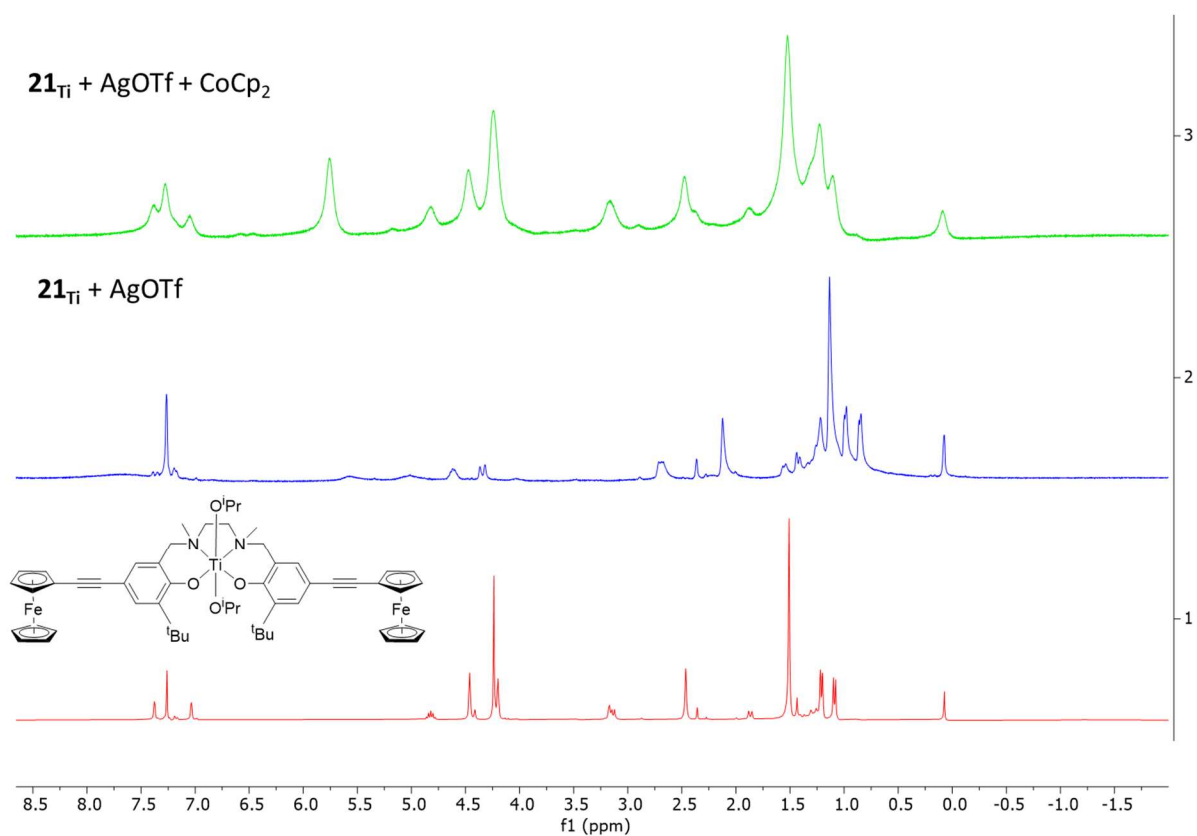


Figure A.58 ¹H NMR (300 MHz, 25 °C, CDCl₃) of **12_{Ti}** (bottom), **12_{Ti-ox}** (middle), and **12_{Ti-red}** (top). **12_{Ti-ox}** was generated by the addition of 2 equivalence of AgOTf to **12** in CDCl₃ in a J. Young NMR tube. **12_{Ti-red}** was generated by the subsequent addition of CoCp₂ to the NMR tube.

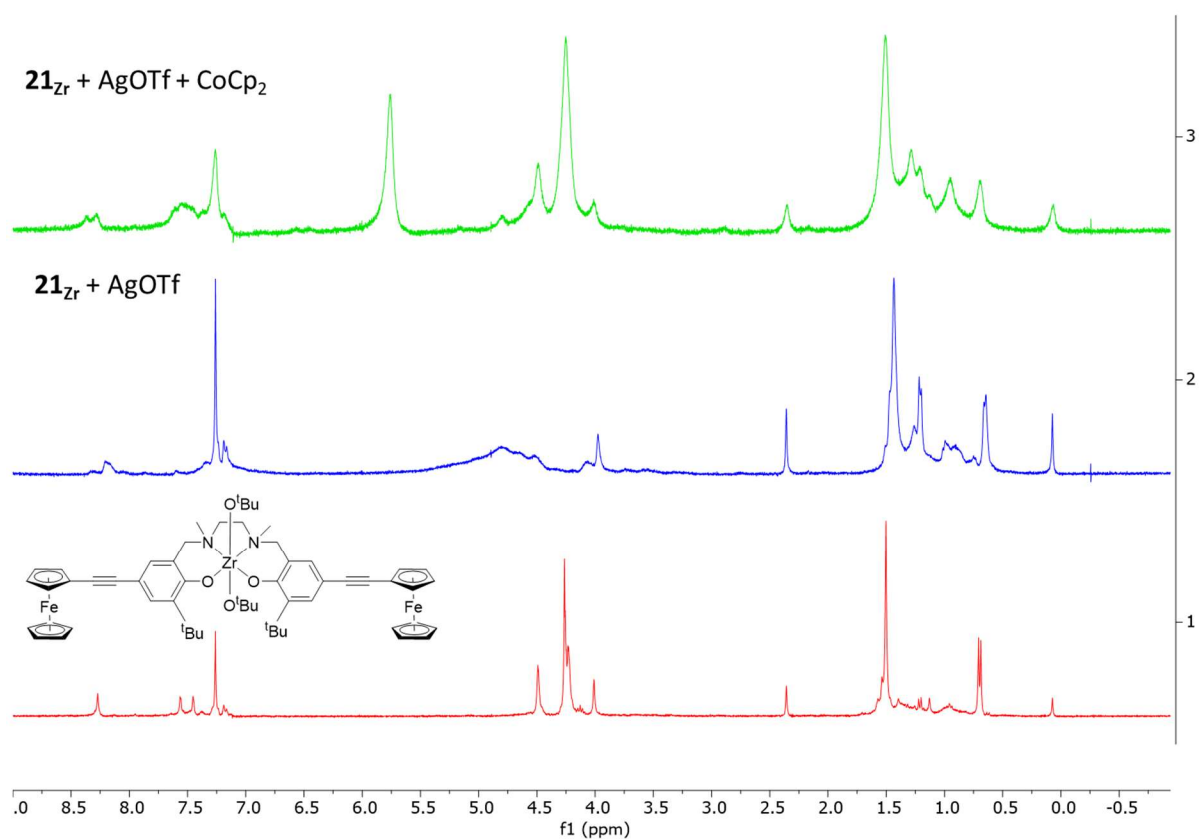


Figure A.59 ^1H NMR spectra (300 MHz, 25 °C, CDCl_3) of 12_{Zr} (bottom), $12_{\text{Zr-ox}}$ (middle), and $12_{\text{Zr-red}}$ (top). $12_{\text{Zr-ox}}$ was generated by the addition of 2 equivalence of AgOTf to 12 in CDCl_3 in a J. Young NMR tube. $12_{\text{Zr-red}}$ was generated by the subsequent addition of CoCp_2 to the NMR tube.

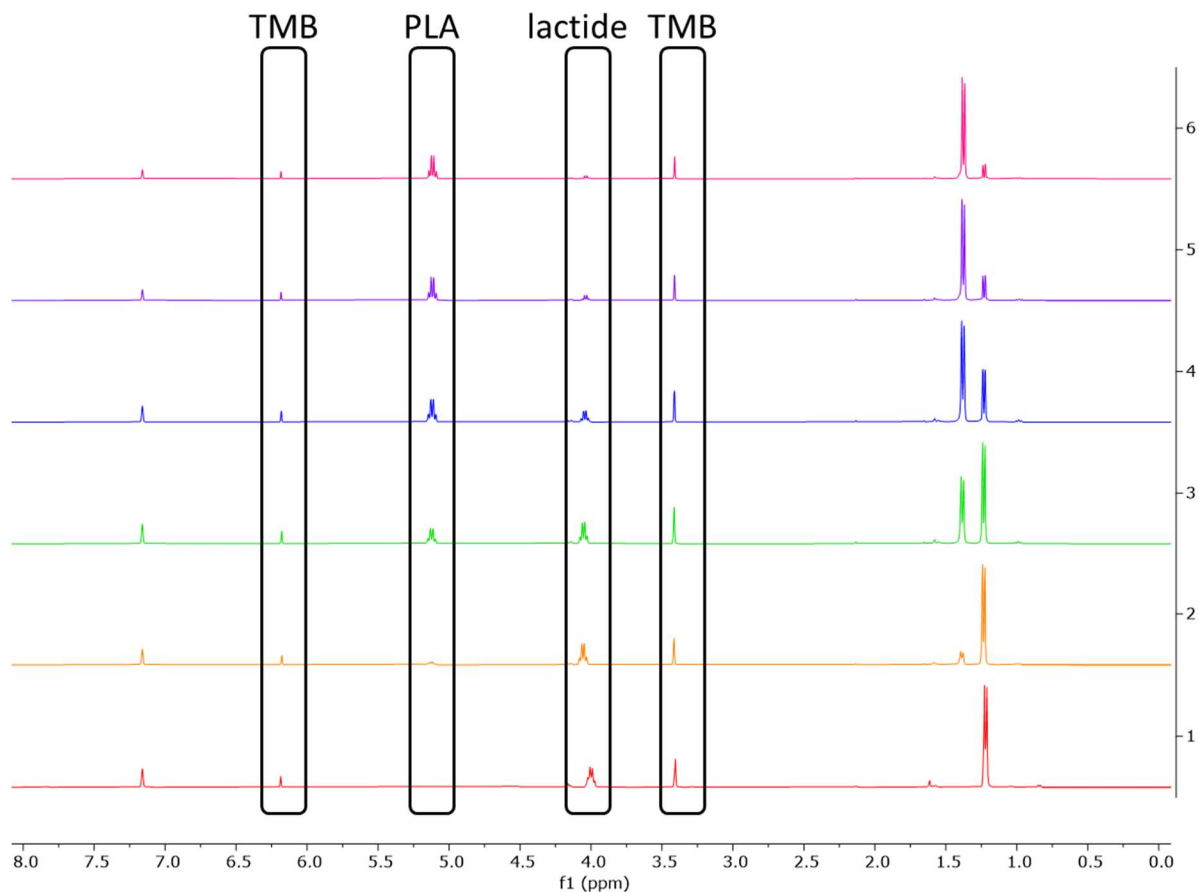


Figure A.60 ^1H NMR spectra (400 MHz, 90 °C, C_6D_6) monitoring the polymerization of L-lactide initiated by catalyst **1_{Ti}**. Each trace represents 2 hours of progression of the reaction starting at 0 hour and ending at 10 hours. The bottom trace (0 hour) shows a large presence of L-lactide with no polymer. The top trace (10 hours) shows L-lactide has been mostly converted to polylactide (PLA). Throughout the 10 hours the amount of internal standard (trimethoxybenzene (TMB)) remained constant.

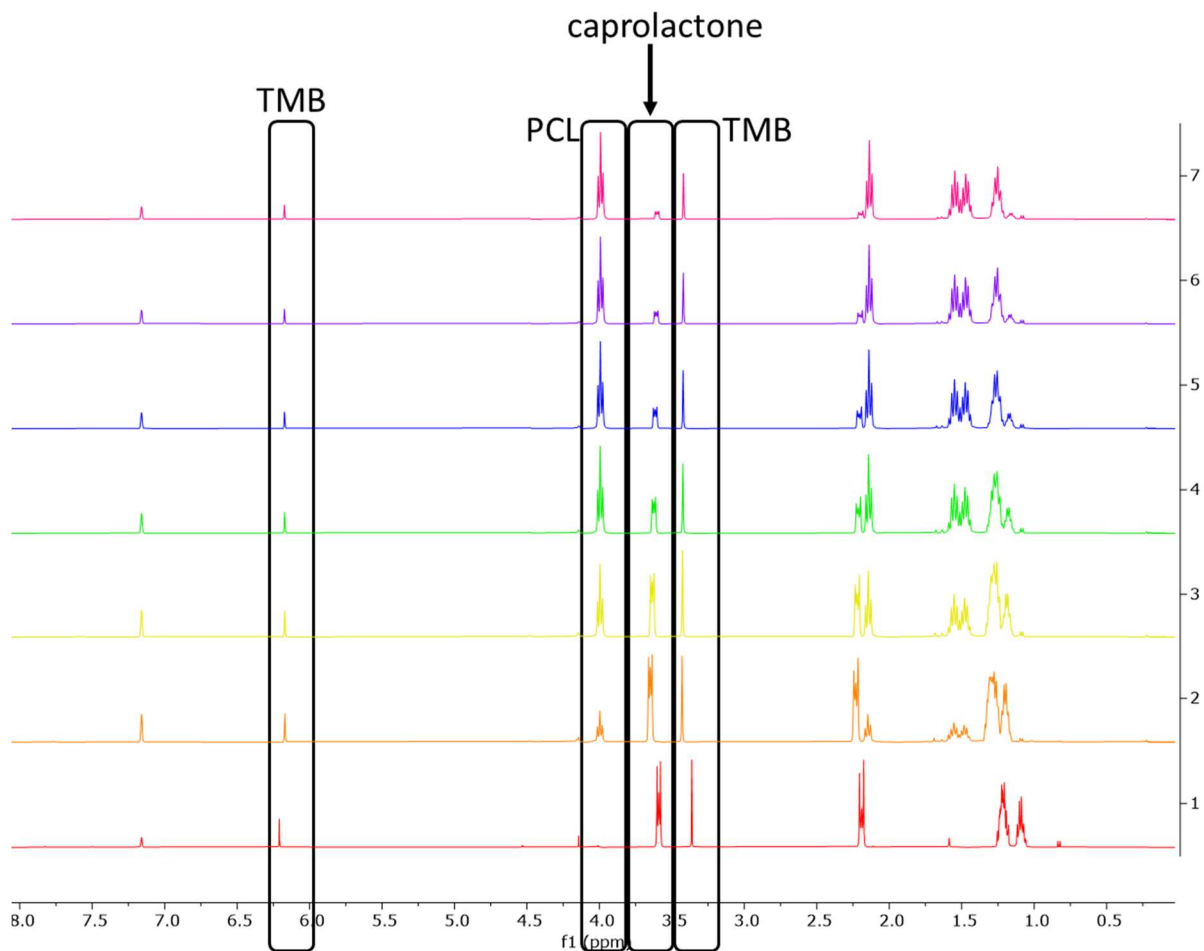


Figure A.61 ¹H NMR spectra (400 MHz, 90 °C, C₆D₆) monitoring the polymerization of ε-caprolactone initiated by catalyst **1_T**. Each trace represents 1 hour of progression of the reaction starting at 0 hour and ending at 6 hours. The bottom trace (0 hour) shows a large presence of ε-caprolactone with no polymer. The top trace (6 hours) shows ε-caprolactone has been mostly converted to polylactide (PLA). Throughout the 6 hours the amount of internal standard (trimethoxybenzene (TMB)) remained constant.

A.4.2 Cyclic Voltammetry

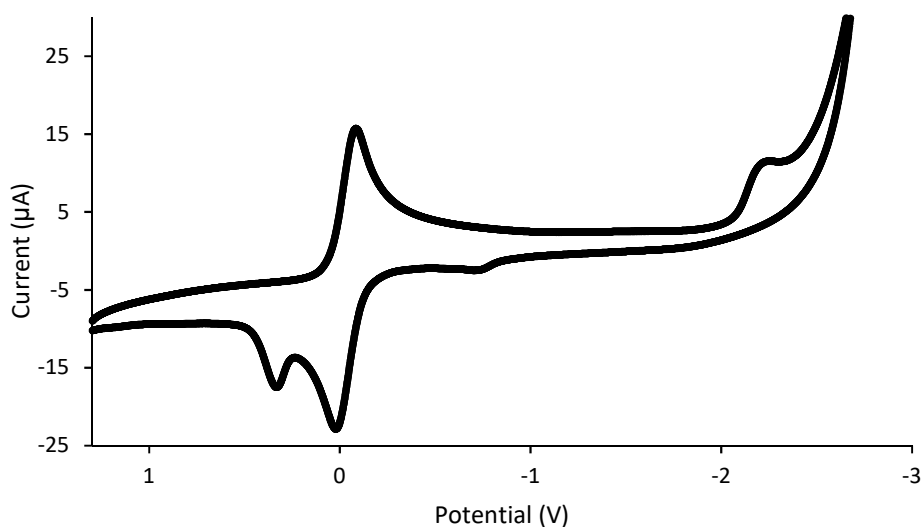


Figure A.62 Cyclic voltammogram of ligand **L12** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), ($E_{1/2} = -0.031$ V) versus Fc/Fc⁺.

A.4.3 Kinetic Study for L-lactide Polymerization

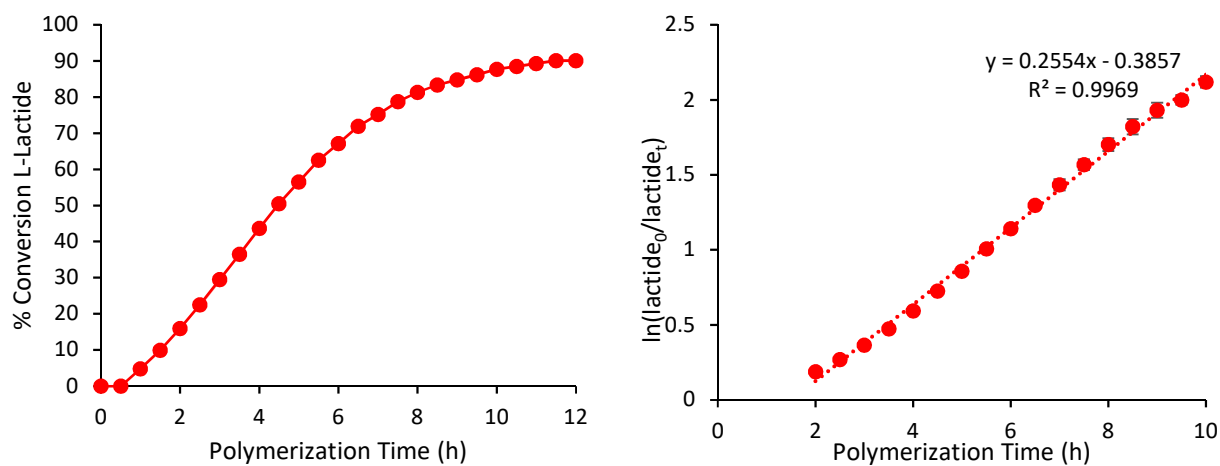


Figure A.63 Polymerization of 100 equivalents of L-lactide in C₆D₆ at 90 °C for **1_{Ti}** (left graph), and a plot of $\ln([L-lactide]_0/[L-lactide]_t)$ vs time (h) to study the polymerization kinetics (right graph).

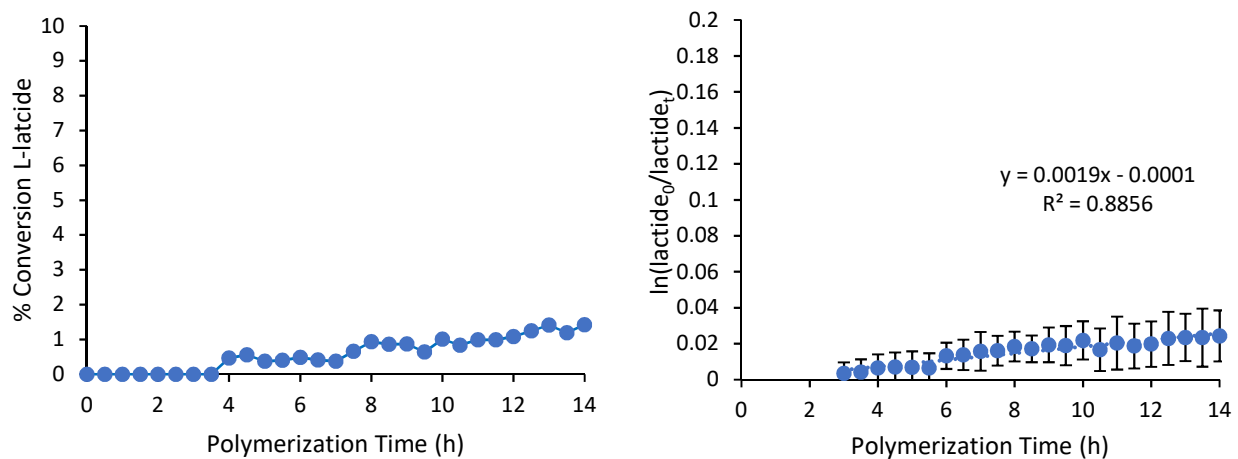


Figure A.64 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for $1_{\text{Ti-ox}}$ (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

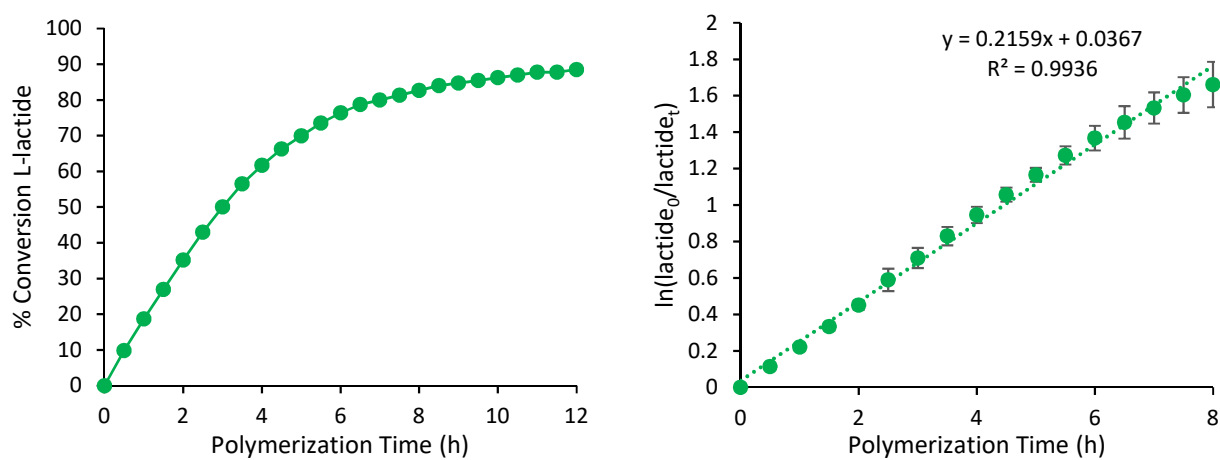


Figure A.65 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for $1_{\text{Ti-red}}$ (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

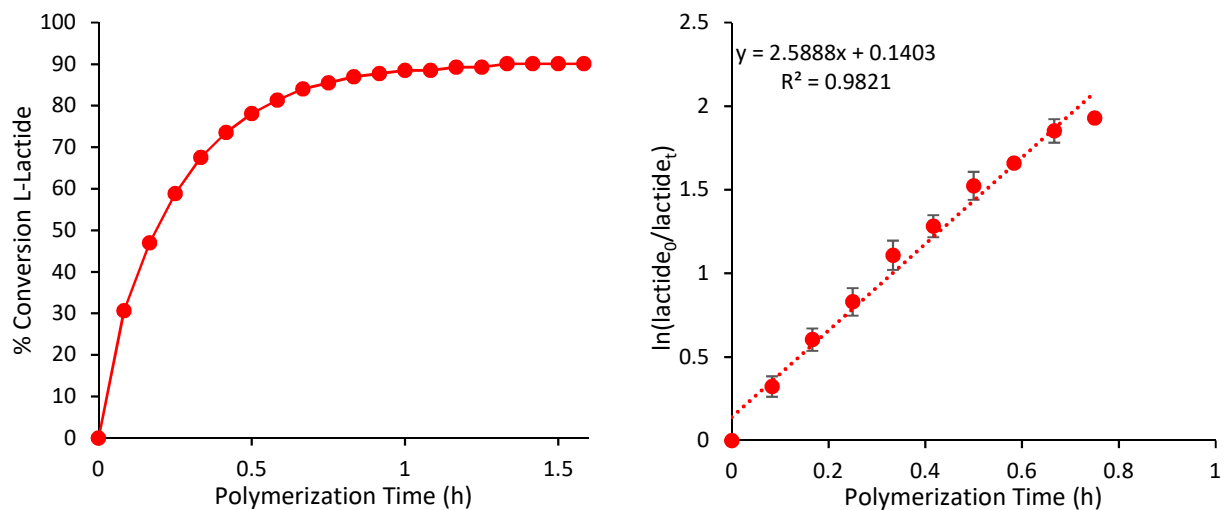


Figure A.66 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for **1Zr** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

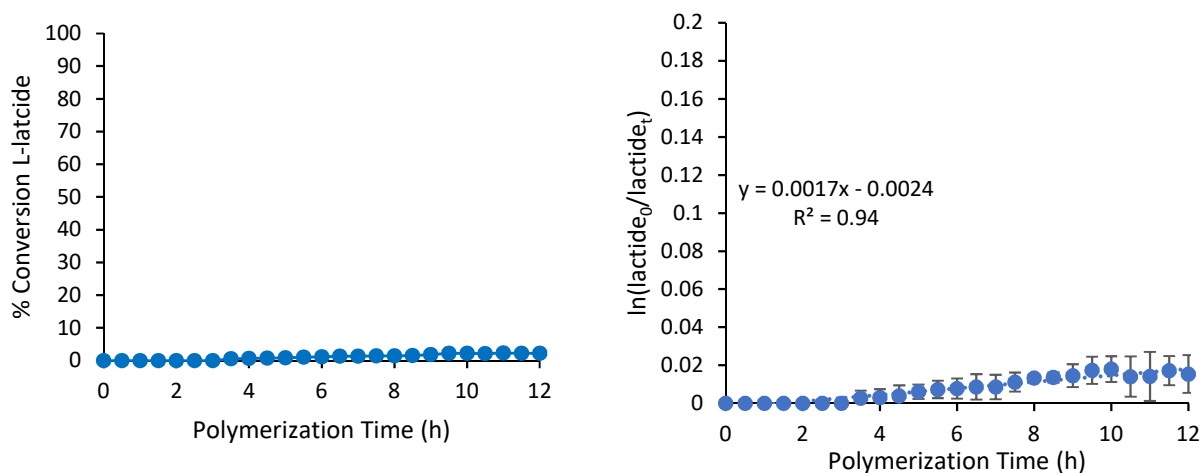


Figure A.67 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for **1Zr-ox** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

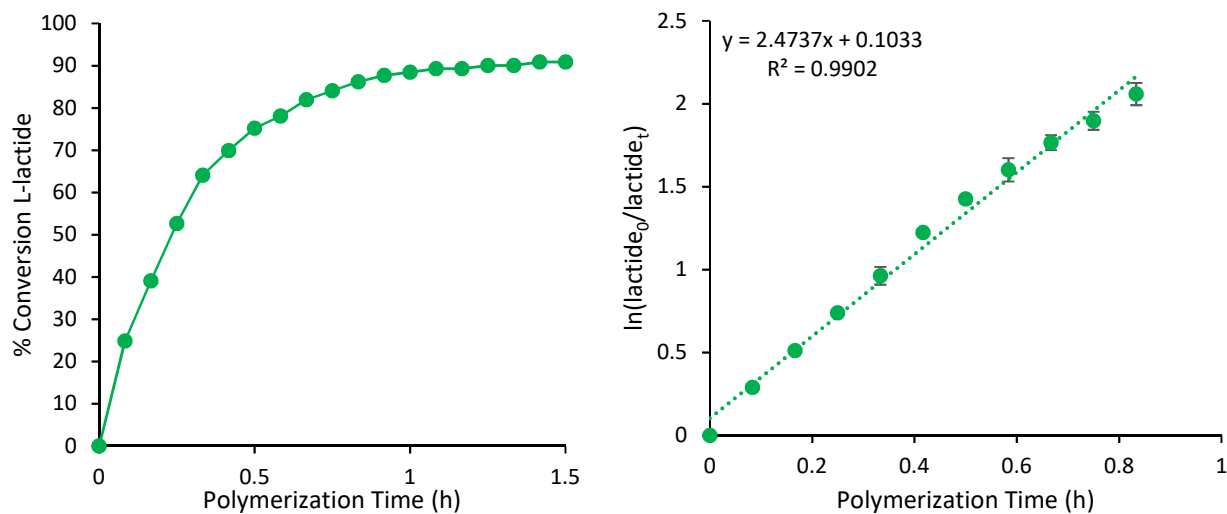


Figure A.68 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for **1Zr-red** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

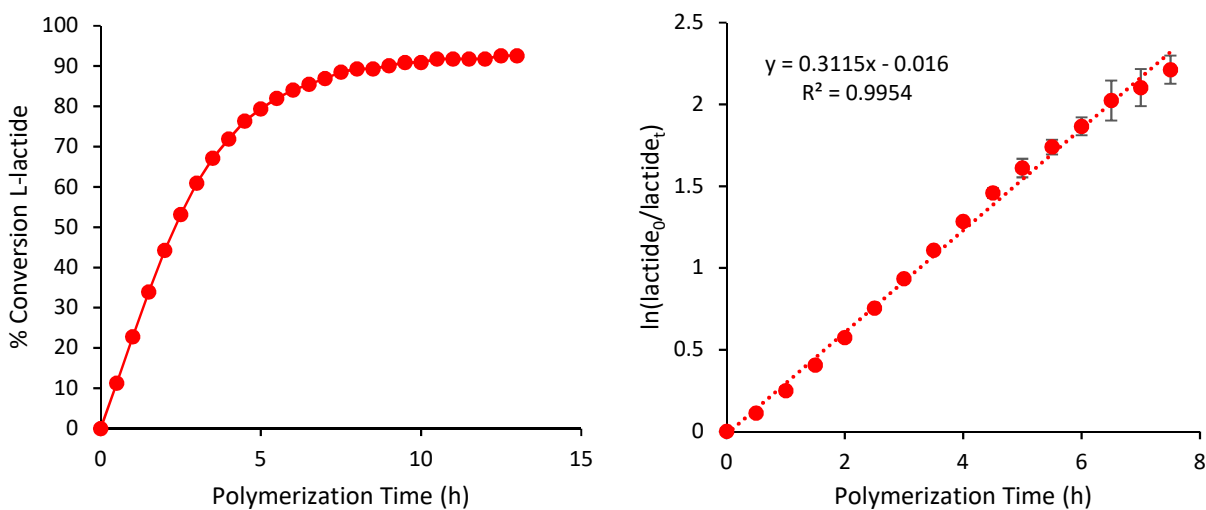


Figure A.69 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for **12Ti** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

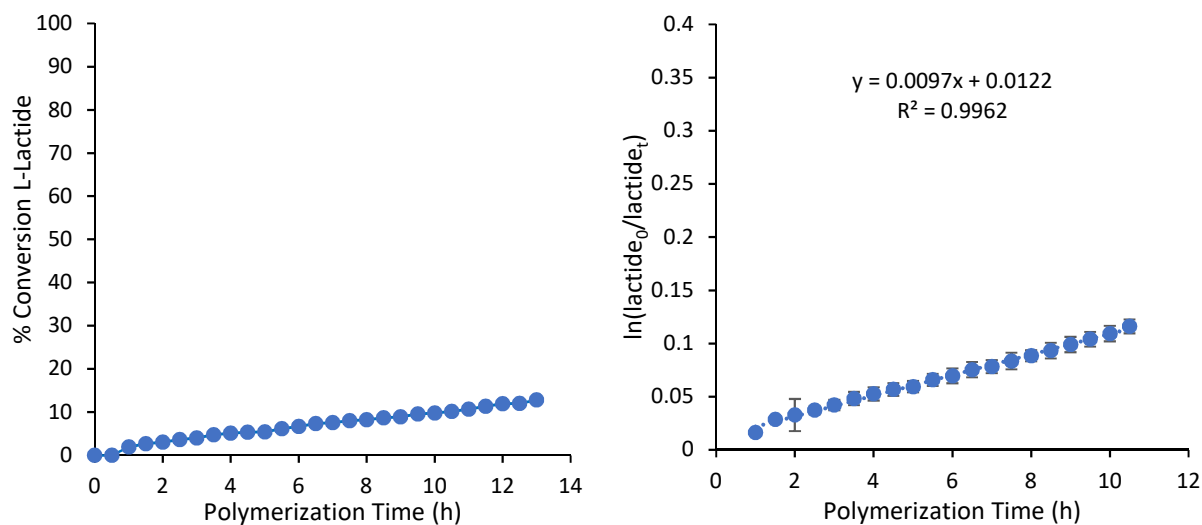


Figure A.70 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for $12_{\text{Ti-ox}}$ (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

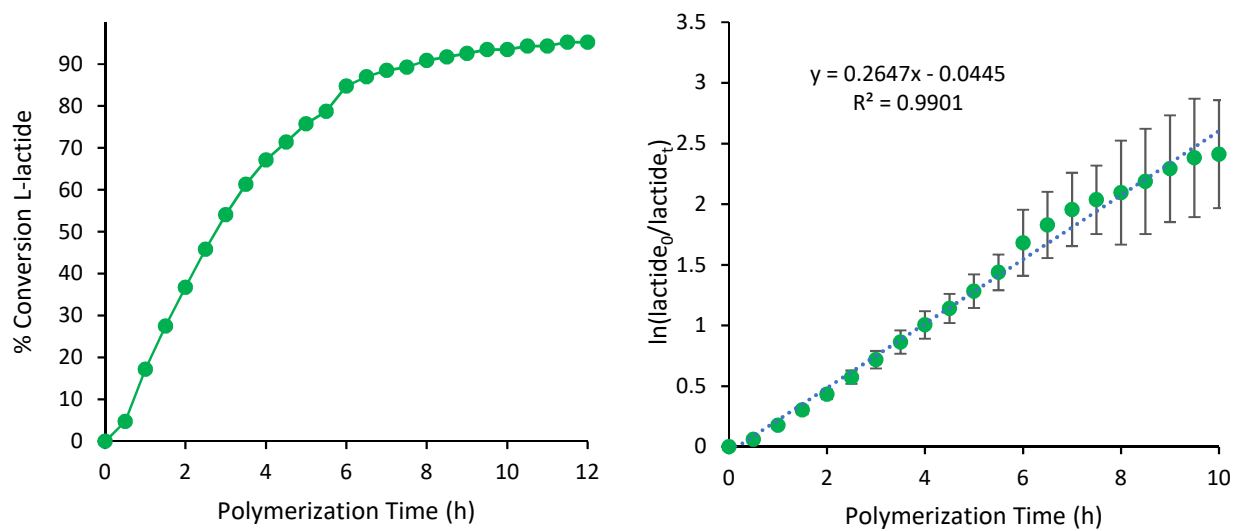


Figure A.71 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for $12_{\text{Ti-red}}$ (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

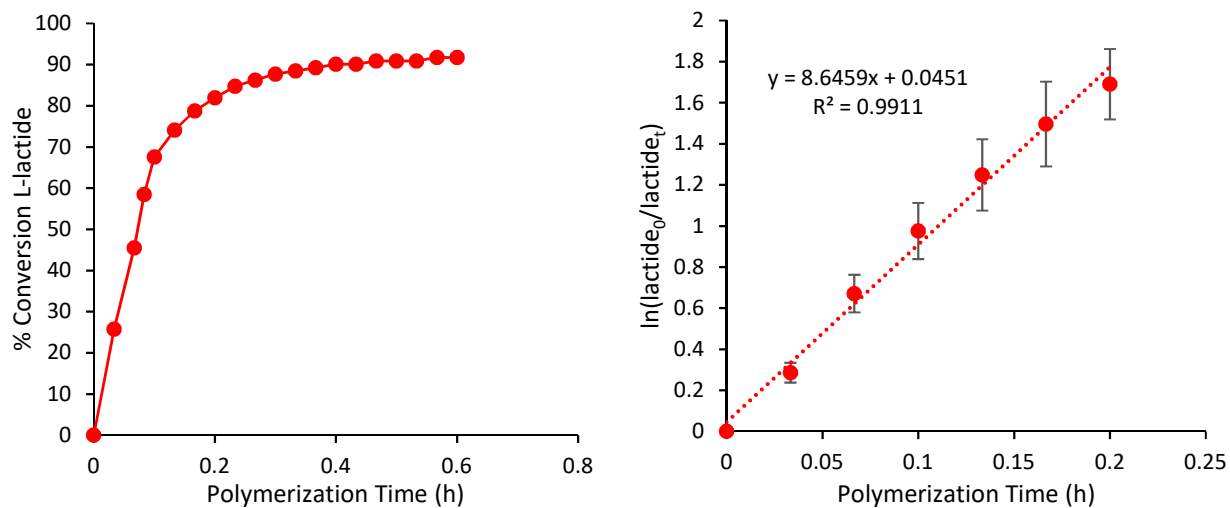


Figure A.72 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for **12_{Zr}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

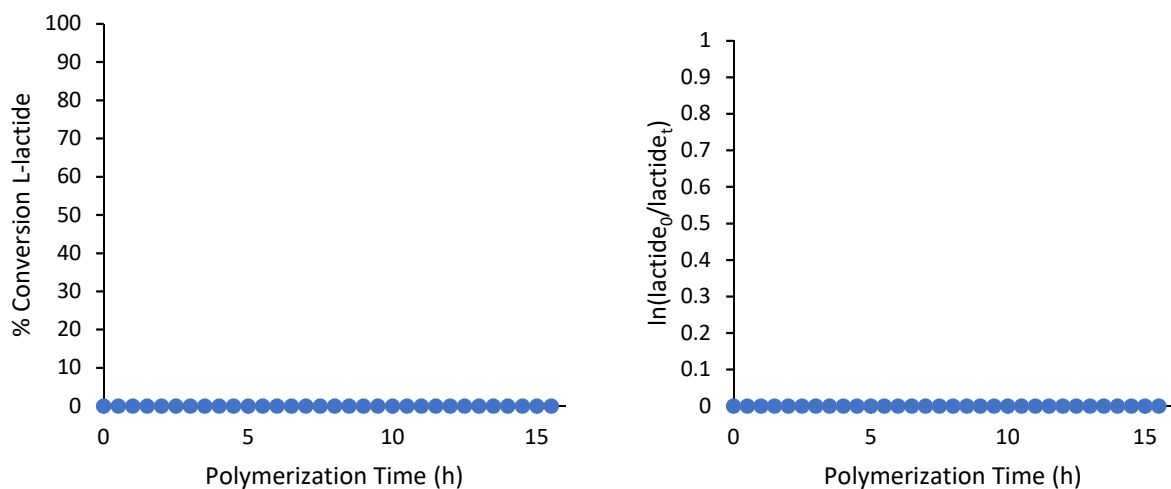


Figure A.73 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for **12_{Zr-ox}** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

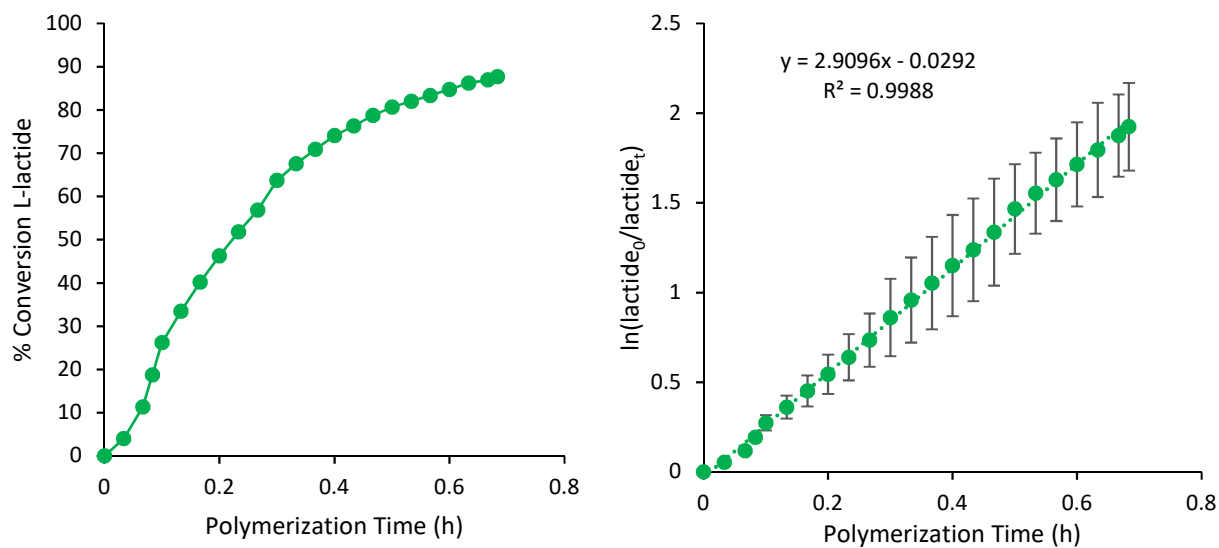


Figure A.74 Polymerization of 100 equivalents of L-lactide in C_6D_6 at 90 °C for **12Zr-red** (left graph), and a plot of $\ln(\text{L-lactide}_0/\text{L-lactide}_t)$ vs time (h) to study the polymerization kinetics (right graph).

A.4.4 Kinetic Study for ϵ -Caprolactone Polymerization

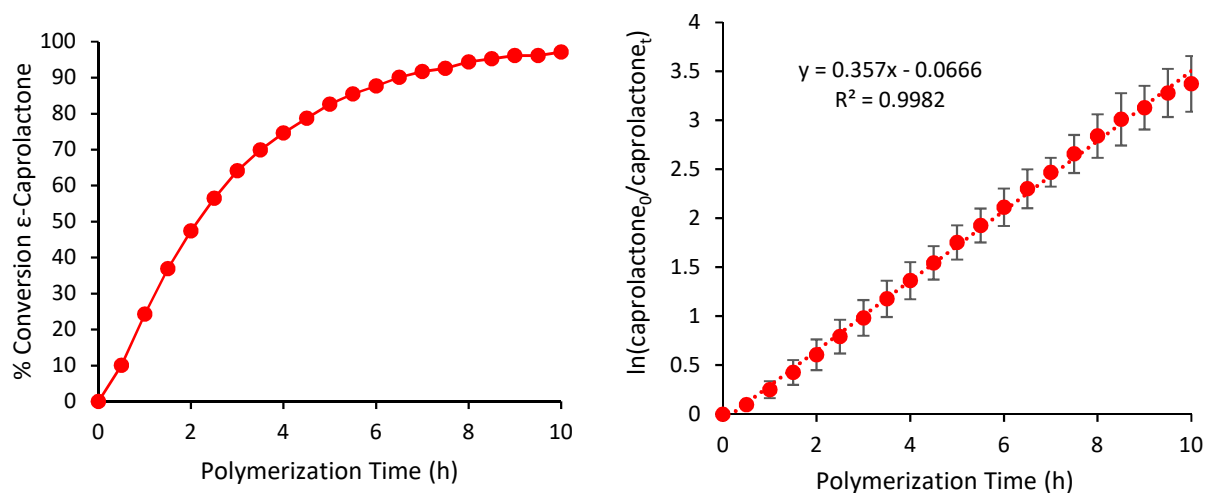


Figure A.75 Polymerization of 100 equivalents of ϵ -caprolactone in C_6D_6 at 90 °C for **1Ti** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

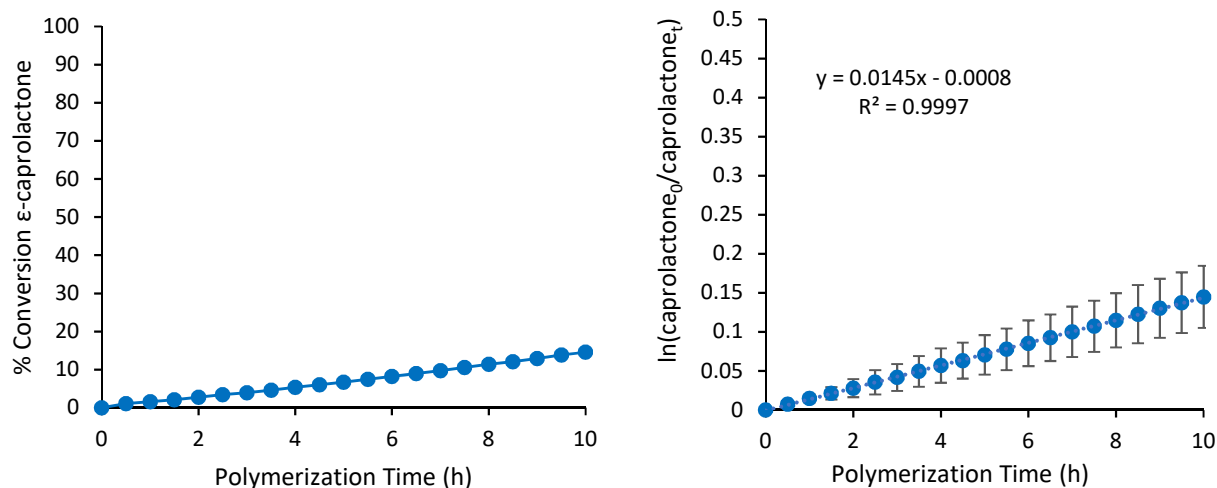


Figure A.76 Polymerization of 100 equivalents of ϵ - caprolactone in C_6D_6 at 90 °C for **1-Ti-ox** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

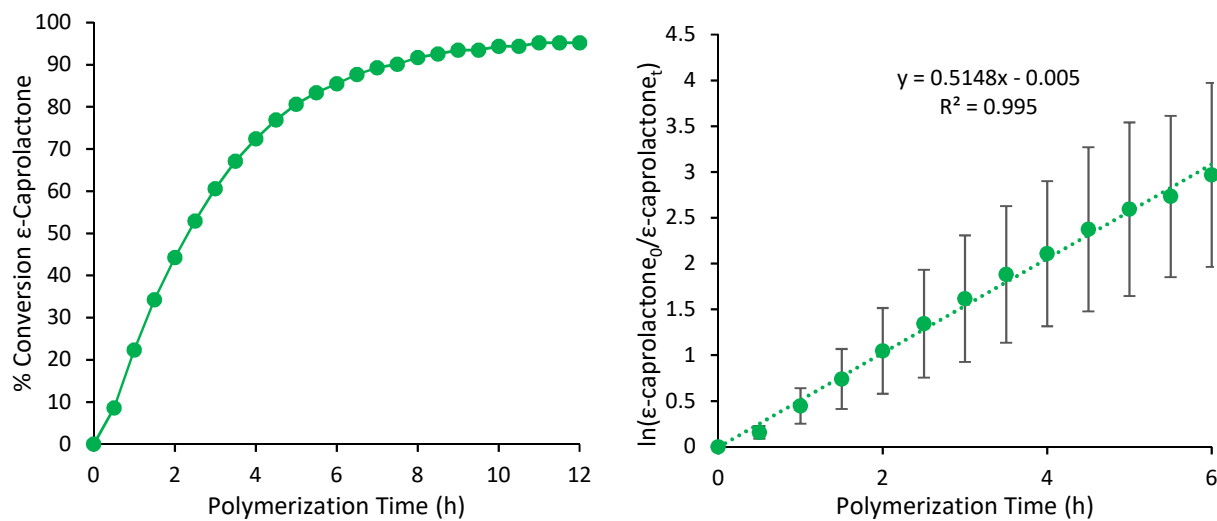


Figure A.77 Polymerization of 100 equivalents of ϵ - caprolactone in C_6D_6 at 90 °C for **1-Ti-ox** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

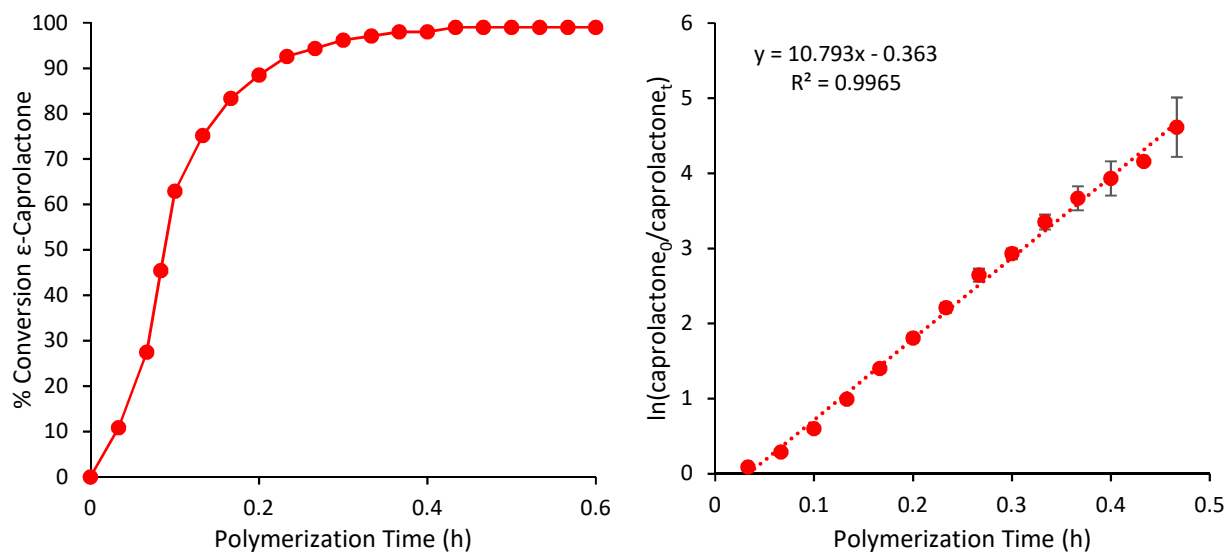


Figure A.78 Polymerization of 100 equivalents of ϵ -caprolactone in C_6D_6 at 90°C for **1_{Zr}** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

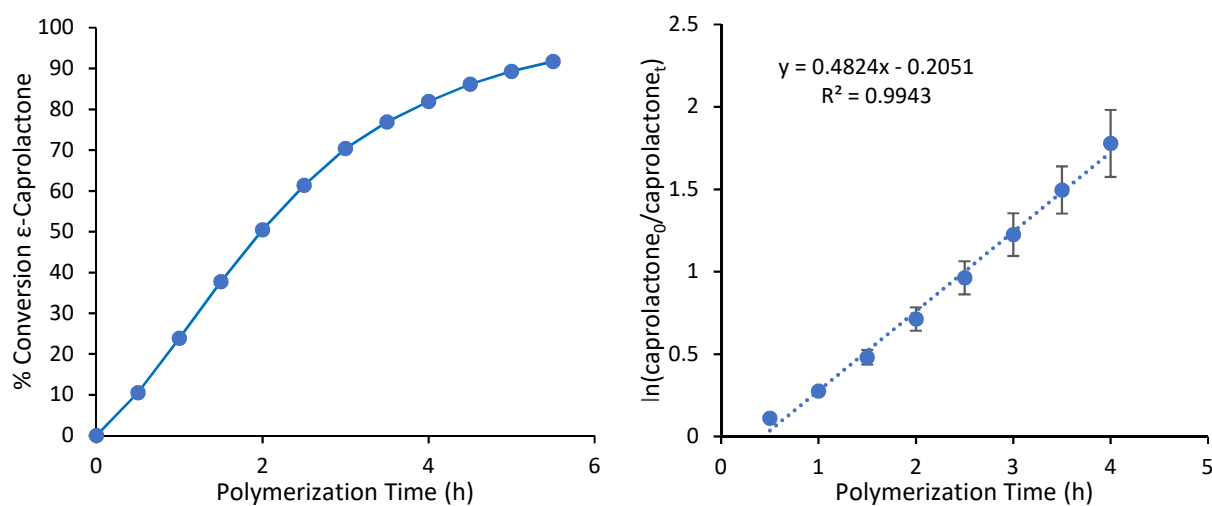


Figure A.79 Polymerization of 100 equivalents of ϵ -caprolactone in C_6D_6 at 90°C for **1_{Zr-ox}** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

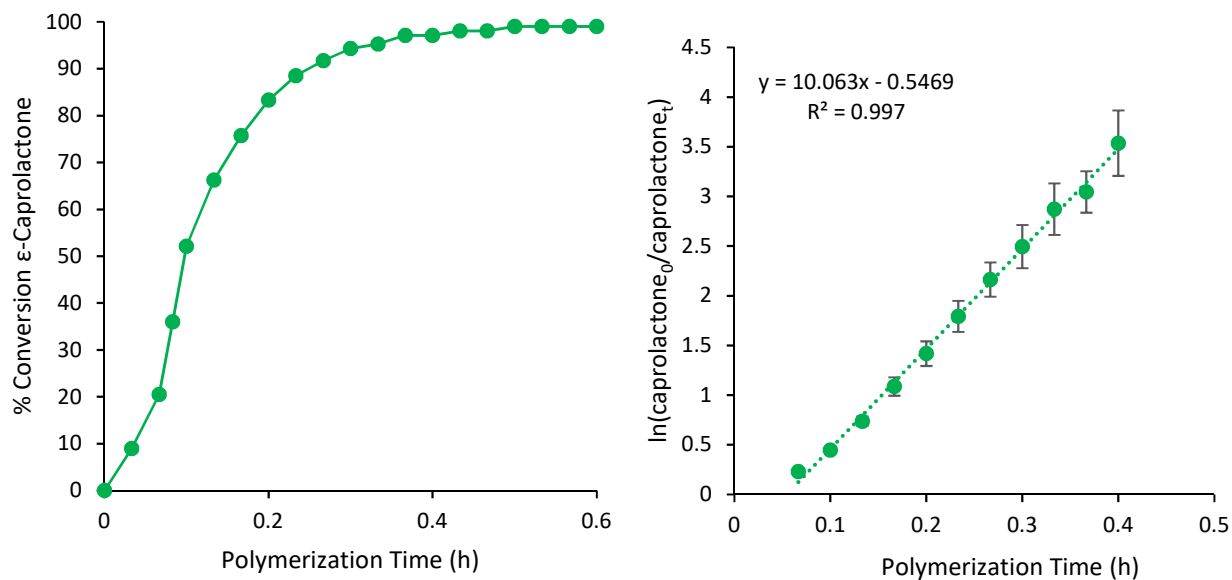


Figure A.80 Polymerization of 100 equivalents of ϵ -caprolactone in C_6D_6 at 90°C for **1Zr-red** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

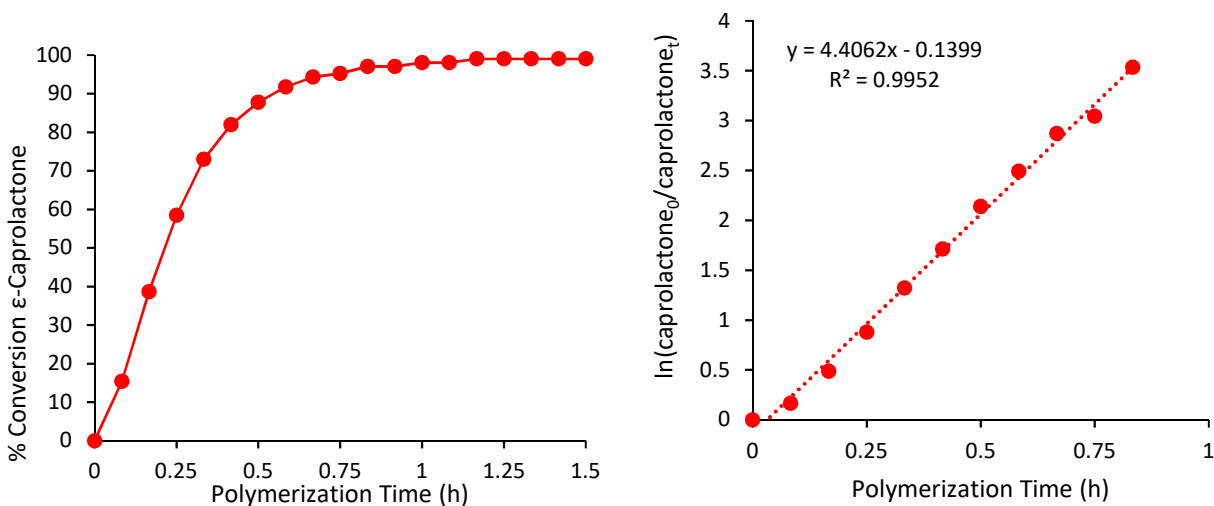


Figure A.81 Polymerization of 100 equivalents of ϵ -caprolactone in C_6D_6 at 90°C for **12Ti** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

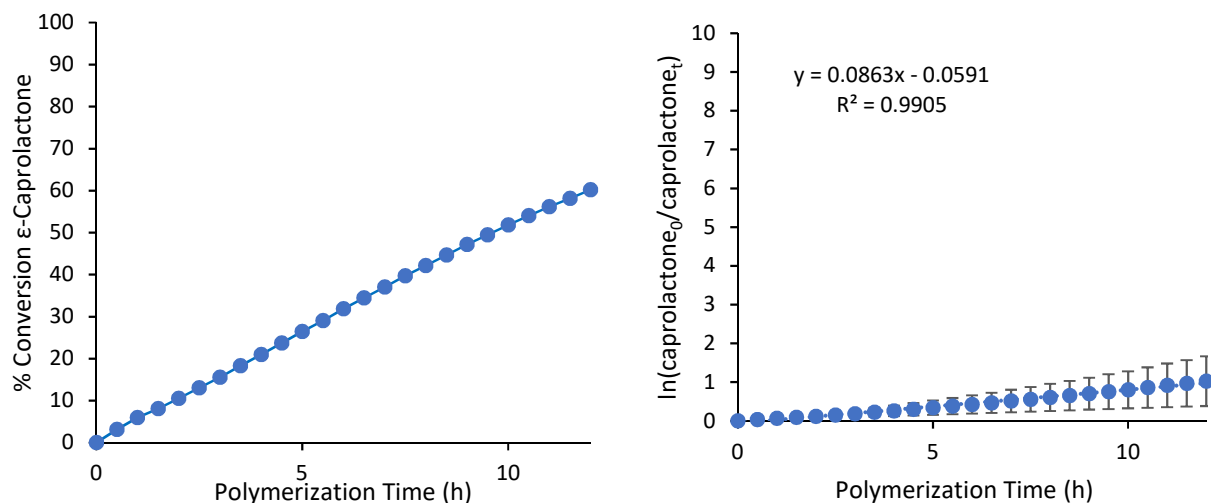


Figure A.82 Polymerization of 100 equivalents of ϵ -caprolactone in C_6D_6 at $90^\circ C$ for **12_{Ti-ox}** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

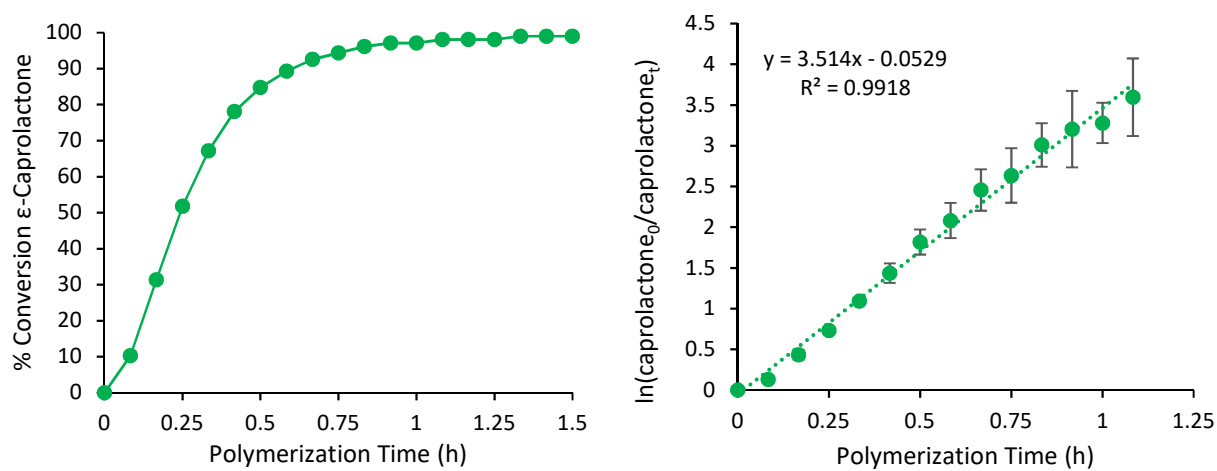


Figure A.83 Polymerization of 100 equivalents of ϵ -caprolactone in C_6D_6 at $90^\circ C$ for **12_{Ti-red}** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

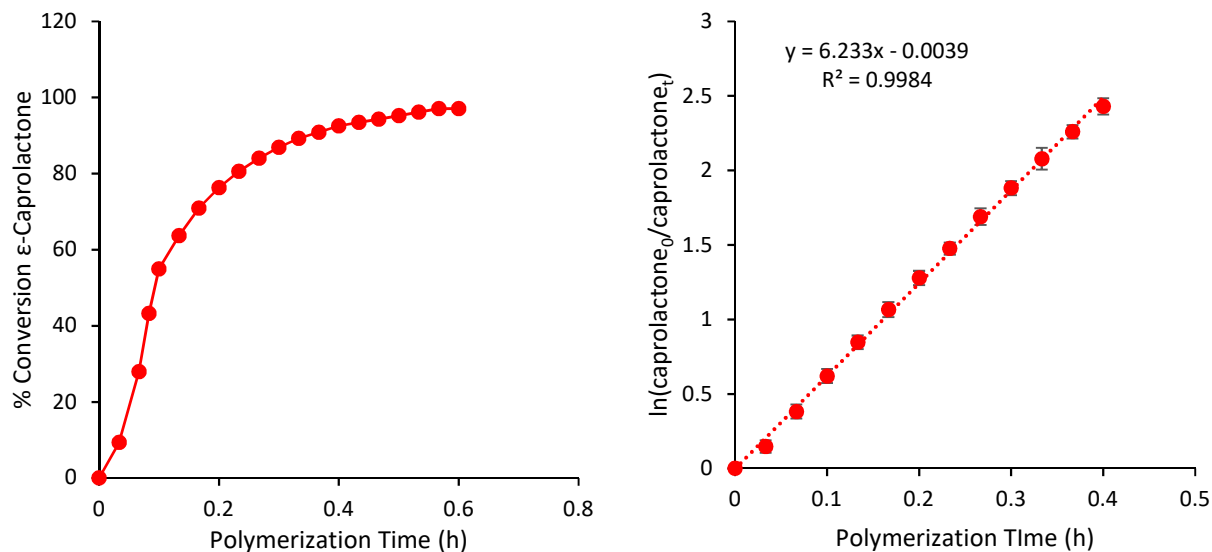


Figure A.84 Polymerization of 100 equivalents of ϵ - caprolactone in C_6D_6 at 90 °C for **12Zr** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

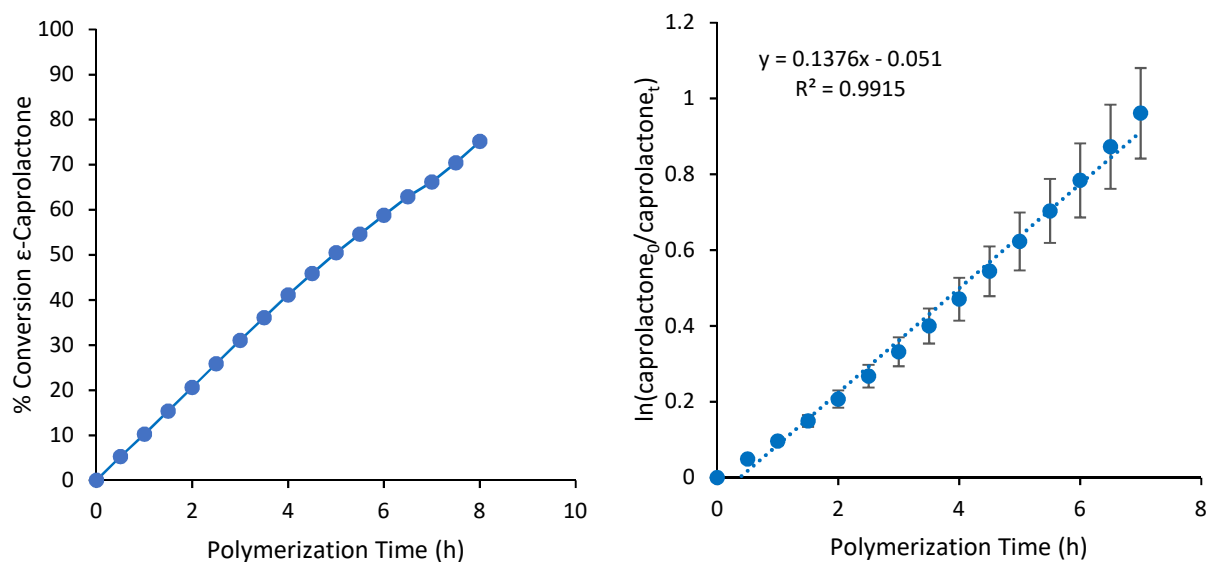


Figure A.85 Polymerization of 100 equivalents of ϵ - caprolactone in C_6D_6 at 90 °C for **12Zr-ox** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

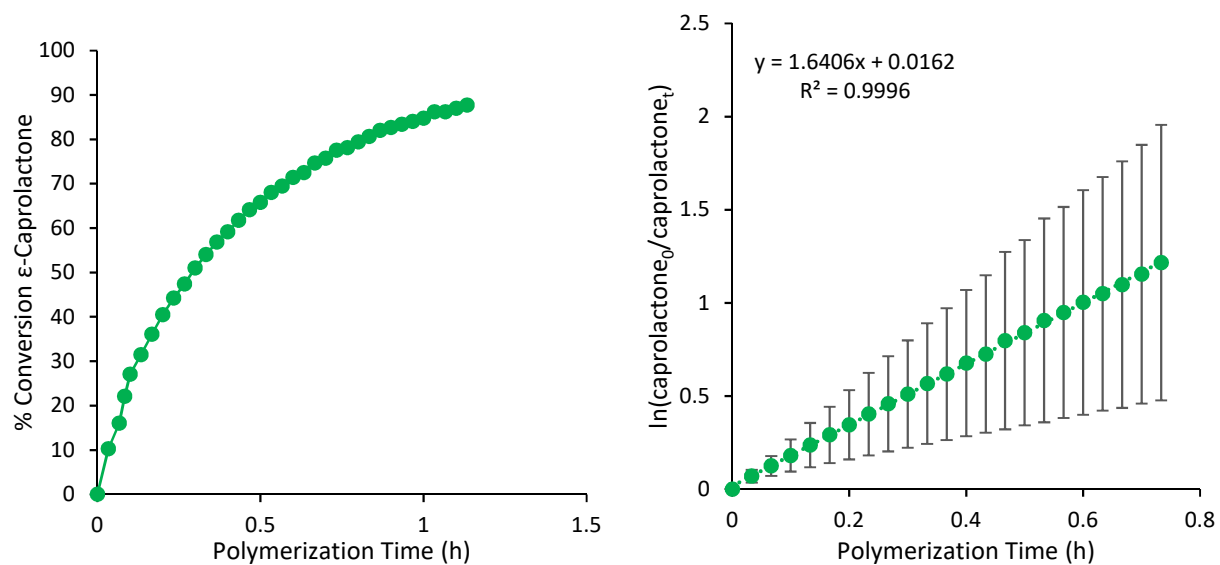


Figure A.86 Polymerization of 100 equivalents of ϵ -caprolactone in C_6D_6 at 90 °C for **12_{Zr-red}** (left graph), and a plot of $\ln(\epsilon\text{-caprolactone}_0/\epsilon\text{-caprolactone}_t)$ vs time (h) to study the polymerization kinetics (right graph).

A.5 Experimental – Chapter 5

A.5.1 General Methods and Materials.

Toluene, DCM, and hexanes were purified using a two-column purification system and degassed via freeze-pump-thaw (x3). All NMR solvents were purchased from Cambridge Isotope Laboratories, and C₆D₆, CDCl₃, and CD₂Cl₂ were dried over activated molecular sieves and degassed prior to use. ¹H and ¹³C NMR spectra were recorded on a Varian 300 or Varian 400 MHz spectrometer. Chemical shifts are reported with respect to solvent residual peaks, 7.26 ppm (CDCl₃), 6.0 ppm (C₂D₂Cl₄), 5.32 ppm (CD₂Cl₂) or 7.16 ppm (C₆D₆). Polyethylene ¹H NMR spectra were recorded at 100 °C on a Varian 400 MHz spectrometer in C₂D₂Cl₄. Branching content was determined using the formula (CH₃/3)/[(CH+CH₂+CH₃)/2]*1000).²²⁷ **13**,¹⁹³ 2,6-diisopropyl-4-nitroaniline,²²¹ 5-methoxyacenaphthoquinone,^{224, 225} **L17**,²⁰⁸ 2,6-diisopropyl-4-methoxyaniline,²²² 5-bromoacenaphthoquinone,²⁴⁶ 4-chloro-2,6-diisopropylaniline¹⁹⁴ and 4-bromo-2,6-di-2-propyl-*N,N*-bis-trimethylsilylaminile²⁴⁷ were synthesized following previously reported procedures. PMAO-IP was purchased from Akzo Nobel and all volatiles were removed under vacuum prior to use. All other reagents were purchased from commercial vendors and used without further purification. All catalyst precursor mass spectrometry analyses were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with DART (direct analysis in real time) ionization source. X-ray diffraction measurements were performed on single crystals Bruker Kappa DUO diffractometer. Cyclic voltammetry measurements were performed on a CH Instruments potentiostat using 0.01 mmol of the compound to be analyzed in 5 mL DCM solution (0.002 M) with supporting electrolyte 0.2 M (*n*Bu)₄NPF₆, using Ag/AgCl as the reference electrode, a gold working electrode, and a tungsten counter electrode at a scanning rate of 100 mV/s⁻¹. All potentials are referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. Molecular weights (M_n) and dispersity (Đ) of the polymers were determined using a Malvern Viscotek HT-GPC equipped with triple detection at 140 °C in 1,2,4-trichlorobenzene at 1.0 mL/min. Polymer melting temperatures (T_m) were measured on a TA instruments Q2000 differential scanning calorimeter on the second heating cycle at a heating rate of 10 °C/min.

A.5.2 Synthesis of 5-nitroacenaphthoquinone (5-No₂ANQ) and 4-nitroacenaphthoquinone (4-No₂ANQ)

Nitroacenaphthoquinone was prepared via a modified literature procedure.²²³⁻²²⁶ To H₂SO₄ (100 mL) was added acenaphthoquinone (6 g, 32.9 mmol). Then concentrated HNO₃ (3.45 mL) was added dropwise and the solution was stirred at room temperature for 3 h, poured over ice, filtered, and washed with water until the solution was no longer acidic. The crude product was purified via silica gel flash column chromatography with 50:50 hexanes:DCM as the eluent. Yield **5-No₂ANQ**: 27.5% (2.0518 g, 9.0 mmol). Yield **4-No₂ANQ**: 11.5 % (0.8574 g, 3.77 mmol). ¹H NMR of **5-No₂ANQ** (300 MHz, 25 °C, CDCl₃), δ, ppm: 8.16 (t, 1H), 8.23 (d, 1H), 8.33 (d, 1H), 8.75 (d, 1H), 9.15 (d, 1H). ¹³C NMR of **5-No₂ANQ** (300 MHz, 25 °C, CDCl₃), δ, ppm: 121.21, 123.95, 126.92, 129.40, 130.58, 132.27, 133.19, 146.20, 186.19, 187.00. HRMS-DART (m/z): [M+H]⁺ calc'd for C₁₂H₅NO₄, 228.02; found, 228.01. ¹H NMR of **4-No₂ANQ** (300 MHz, 25 °C, CDCl₃), δ, ppm: 8.07 (t, 1H), 8.35 (d, 1H), 8.54 (d, 1H), 8.87 (s, 1H), 9.27 (s, 1H). ¹³C NMR of **4-No₂ANQ** (300 MHz, 25 °C, CDCl₃), δ, ppm: 116.22, 125.92, 128.64, 129.23, 129.98, 130.24, 130.92, 132.32, 134.88, 146.71, 186.13, 187.19. HRMS-DART (m/z): [M+H]⁺ calc'd for C₁₂H₅NO₄, 228.02; found, 228.01.

A.5.3 Synthesis of $C_{36}H_{39}N_3O_2$ (**L14**)

To MeOH (20 mL) was added 5-nitroacenaphthoquinone (0.5 g, 2.2 mmol), 2,6-diisopropylaniline (0.87 mL, 4.6 mmol), and formic acid (0.33 mL, 8.8 mmol). The reaction was heated at reflux for 24 h, cooled to RT, filtered, and washed with MeOH, to yield **L14** as a red solid. Yield: 65% (0.78 g, 1.4 mmol). 1H NMR of (300 MHz, $25^\circ C$, $CDCl_3$), δ , ppm: 0.97 (d, 12H), 1.24 (d, 12H), 2.95 (m, 4H), 6.68 (d, 1H), 6.79 (d, 1H), 7.29 (s, 6H), 7.63 (t, 1H), 8.28 (d, 1H), 8.76 (d, 1H). ^{13}C NMR of (300 MHz, $25^\circ C$, $CDCl_3$), δ , ppm: 23.07, 23.34, 28.78, 121.86, 123.73, 123.80, 124.81, 125.08, 126.40, 126.52, 129.73, 131.57, 134.45, 134.90, 135.02, 145.14, 146.90, 159.02. HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{36}H_{39}N_3O_2$, 546.30; found, 546.28.

A.5.4 Synthesis of $C_{36}H_{39}N_3O_2Br_2Ni$ (**14**)

Under an inert atmosphere, (DME)NiBr₂ (0.113 g, 0.37 mmol) in DCM (5 mL) was added to **L14** (0.2 g, 0.37 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **14**. Yield: 65% (0.185 g, 0.24 mmol). Crystals suitable for X-ray crystallography were obtained by crystallization from DCM with pentanes via layering. 1H NMR of (300 MHz, $25^\circ C$, CD_2Cl_2), δ , ppm: -16.11, -15.67, 1.53, 2.12, 3.33, 3.49, 5.88, 18.50, 23.75. HRMS-DART (m/z): $[M-Br]^+$ calc'd for $C_{36}H_{39}N_3O_2BrNi$, 684.32; found, 684.10.

A.5.5 Synthesis of $C_{36}H_{38}N_4O_4$ (**L15**)

To a round bottom flask equipped with a Soxhlet and condenser was added acenaphthoquinone (0.22 g, 1.2 mmol), 2,6-diisopropyl-4-nitroaniline (0.59 g, 2.7 mmol), *p*-toluene sulfonic acid (0.011 g, 0.06 mmol), and dry toluene (16 mL). The reaction was allowed to reflux for 2 days, cool to RT, and then all volatiles were removed under reduced pressure. The resulting yellow solid was washed with Et₂O to yield **L15**. Yield: 49% (0.3453 g, 0.58 mmol). 1H NMR of (300 MHz, $25^\circ C$, $CDCl_3$), δ , ppm: 1.06 (d, 12H), 1.27 (d, 12H), 2.99 (br, 4H), 6.82 (br, 2H), 7.5 (t, 2H), 8.01 (d, 2H), 8.18 (s, 4H). ^{13}C NMR of (300 MHz, $25^\circ C$, $CDCl_3$), δ , ppm: 22.70, 23.05, 29.17, 119.87, 123.47, 128.50, 130.33, 131.44, 136.96, 141.35, 145.28, 153.04, 160.26. HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{36}H_{38}N_4O_4$, 591.29; found, 591.25.

A.5.6 Synthesis of $C_{36}H_{38}N_4O_4Br_2Ni$ (**15**)

Under an inert atmosphere, (DME)NiBr₂ (0.1009 g, 0.33 mmol) in DCM (5 mL) was added to **L15** (0.1932 g, 0.33 mmol) in DCM (5 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **15**. Yield: 59% (0.1577 g, 0.1947 mmol). 1H NMR of (300 MHz, $25^\circ C$, CD_2Cl_2), δ , ppm: 1.07, 1.21, 1.84, 2.28, 6.03, 8.16, 16.91, 21.72, 24.11. HRMS-DART (m/z): $[M-Br]^+$ calc'd for $C_{36}H_{38}N_4O_4BrNi$, 729.32; found, 729.07.

A.5.7 Synthesis of $C_{36}H_{37}N_5O_6$ (**L16**)

To a round bottom flask equipped with a Soxhlet and condenser was added 5-nitroacenaphthoquinone (0.26 g, 1.14 mmol), 2,6-diisopropyl-4-nitroaniline (0.5596 g, 2.52 mmol), *p*-toluene sulfonic acid (0.014 g, 0.074 mmol), and dry toluene (16 mL). The reaction was allowed to reflux for 2 days, cool to RT, and then all volatiles were removed under reduced pressure. The resulting red solid was washed with Et₂O to yield **L16**. Yield: 75%

(0.5685 g, 0.1937 mmol). ^1H NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 1.11 (s, 12H), 1.26 (s, 12H), 2.90 (s, 4H), 6.92 (br, 2H), 7.78 (br, 1H), 8.17 (s, 4H), 8.42 (br, 1H), 8.88 (d, 1H). ^{13}C NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 22.80, 22.92, 29.22, 29.34, 119.94, 121.84, 124.29, 124.88, 126.97, 127.88, 132.11, 136.57, 141.90, 145.55, 145.97, 152.20, 158.63. HRMS-DART (m/z): $[\text{M}+\text{H}]^+$ calc'd for $\text{C}_{36}\text{H}_{37}\text{N}_5\text{O}_6$, 636.27; found, 636.23.

A.5.8 Synthesis of $\text{C}_{36}\text{H}_{37}\text{N}_5\text{O}_6\text{Br}_2\text{Ni}$ (**16**)

Under an inert atmosphere, (DME)NiBr₂ (0.097 g, 0.31 mmol) in DCM (5 mL) was added to **L16** (0.2 g, 0.31 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **16**. Yield: 87 % (0.2314 g, 0.27 mmol). ^1H NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 0.52, 1.09, 1.24, 1.95, 2.28, 2.85, 3.32, 6.28, 6.89, 7.80, 8.16, 8.84. HRMS-DART (m/z): $[\text{M}-\text{NiBr}_2]^+$ calc'd for $\text{C}_{36}\text{H}_{37}\text{N}_5\text{O}_6$, 636.27; found, 636.23.

A.5.9 Synthesis of $\text{C}_{37}\text{H}_{42}\text{N}_2\text{OBr}_2\text{Ni}$ (**17**)

Under an inert atmosphere, a (DME)NiBr₂ (0.145 g, 0.47 mmol) solution in DCM (5 mL) was added to **L17** (0.25 g, 0.47 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **17**. Yield: 85 % (0.3037 g, 0.40 mmol). Crystals suitable for X-ray crystallography were obtained by crystallization from DCM with pentane via layering. ^1H NMR of (300 MHz, 25 °C, CD_2Cl_2), δ , ppm: -15.91, -15.39, 1.34, 1.54, 2.05, 3.09, 5.62, 5.97, 16.89, 23.57, 23.86, 24.41, 24.67. HRMS-DART (m/z): $[\text{M}-\text{Br}]^+$ calc'd for $\text{C}_{37}\text{H}_{42}\text{N}_2\text{OBrNi}$, 669.35; found, 669.13.

A.5.10 Synthesis of $\text{C}_{38}\text{H}_{44}\text{N}_2\text{O}_2$ (**L18**)

To a round bottom flask equipped with a Soxhlet and condenser was added acenaphthoquinone (0.1275 g, 0.7 mmol), 2,6-diisopropyl-4-methoxyaniline (0.3195 g, 1.54 mmol), *p*-toluene sulfonic acid (0.015 g, 0.077 mmol), and dry toluene (16 mL). The reaction was allowed to reflux for 2 days, cool to RT, and then all volatiles were removed under reduced pressure. The resulting red solid was washed with Et₂O to yield **L18**. Yield: 99% (0.388 g, 0.69 mmol). ^1H NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 0.95 (d, 12H), 1.24 (d, 12H), 3.02 (m, 4H), 3.92 (s, 6H), 6.74 (d, 2H), 6.84 (s, 4H), 7.38 (t, 2H), 7.88 (d, 2H). ^{13}C NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 23.06, 23.29, 28.76, 55.28, 108.95, 123.24, 127.84, 128.78, 129.52, 131.12, 136.86, 140.71, 141.17, 156.73, 161.90. HRMS-DART (m/z): $[\text{M}+\text{H}]^+$ calc'd for $\text{C}_{38}\text{H}_{44}\text{N}_2\text{O}_2$, 561.34; found, 561.31.

A.5.11 Synthesis of $\text{C}_{38}\text{H}_{44}\text{N}_2\text{O}_2\text{Br}_2\text{Ni}$ (**18**)

Under an inert atmosphere, a (DME)NiBr₂ (0.110 g, 0.36 mmol) solution in DCM (5 mL) was added to **L18** (0.2 g, 0.36 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **18**. Yield: 70 % (0.1949 g, 0.25 mmol). ^1H NMR of (300 MHz, 25 °C, CD_2Cl_2), δ , ppm: 1.33, 1.77, 5.83, 8.69, 17.14, 21.92, 24.65. HRMS-DART (m/z): $[\text{M}-\text{Br}]^+$ calc'd for $\text{C}_{38}\text{H}_{44}\text{N}_2\text{O}_2\text{BrNi}$, 699.38; found, 699.13.

A.5.12 Synthesis of $C_{39}H_{46}N_2O_3$ (**L19**)

To MeOH (20 mL) was added 5-methoxyacenaphthoquinone (0.1485 g, 0.70 mmol), 2,6-diisopropyl-4-methoxyaniline (0.3195 g, 1.54 mmol), and formic acid (0.1 mL, 2.8 mmol). The reaction was heated at reflux for 24 h, cool to RT, and then all volatiles were removed under reduced pressure. Then purified via silica gel chromatography using hexanes: ethyl acetate (95:5) as an eluent to yield **L19** as a red solid. Yield: 66% (0.27 g, 0.46 mmol). 1H NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 0.95 (t, 12H), 1.21 (d, 12H), 3.02 (m, 4H), 3.90 (s, 6H), 3.96 (s, 3H), 6.70 (m, 3H), 6.83 (s, 4H), 7.31 (t, 1H), 8.08 (d, 1H). ^{13}C NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 23.07, 23.13, 23.29, 23.39, 28.69, 28.74, 55.26, 55.31, 55.85, 105.60, 108.90, 122.70, 123.03, 123.82, 124.15, 124.95, 126.83, 128.92, 136.86, 137.19, 141.21, 141.43, 142.35, 156.53, 156.66, 157.35, 161.22, 162.60. HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{39}H_{46}N_2O_3$, 591.35; found, 591.32.

A.5.13 Synthesis of $C_{39}H_{46}N_2O_3Br_2Ni$ (**19**)

Under an inert atmosphere, (DME)NiBr₂ (0.104 g, 0.34 mmol) in DCM (5 mL) was added to **L19** (0.200 g, 0.34 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **19**. Yield: 55 % (0.152 g, 0.187 mmol). Crystals suitable for X-ray crystallography were obtained by crystallization from DCM with pentane via vapor diffusion. 1H NMR of (300 MHz, 25 °C, CD_2Cl_2), δ , ppm: 1.33, 1.82, 3.13, 5.66, 6.00, 8.85, 16.98, 22.33, 22.58, 24.40, 24.79. HRMS-DART (m/z): $[M-Br]^+$ calc'd for $C_{39}H_{46}N_2O_3BrNi$, 729.41; found, 729.15.

A.5.14 Synthesis of $C_{36}H_{39}N_3O_2$ (**L20**)

To MeOH (80 mL) was added 4-nitroacenaphthoquinone (0.50 g, 2.2 mmol), 2,6-diisopropylaniline (0.87 mL, 4.6 mmol), and formic acid (0.33 mL, 8.8 mmol). The reaction was heated at reflux for 24 h, cooled to RT, filtered, and washed with MeOH, to yield **L20** as a red solid. Yield: 54% (0.6482 g, 1.19 mmol). 1H NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 0.97 (d, 12H), 1.24 (d, 12H), 2.98 (m, 4H), 6.81 (d, 1H), 7.29-7.34 (m, 7H), 7.54 (t, 1H), 8.09 (d, 1H), 8.85 (s, 1H). ^{13}C NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 23.23, 23.37, 23.47, 28.86, 117.08, 123.83, 124.04, 124.92, 125.42, 126.77, 129.83, 129.91, 130.16, 130.73, 131.02, 135.01, 135.24, 142.20, 146.77, 147.11, 147.45, 159.54, 159.87. HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{36}H_{38}N_3O_2$, 546.30; found, 546.26.

A.5.15 Synthesis of $C_{36}H_{39}N_3O_2Br_2Ni$ (**20**)

Under an inert atmosphere, (DME)NiBr₂ (0.1414 g, 0.46 mmol) in DCM (5 mL) was added to **L20** (0.2507 g, 0.46 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **20**. Yield: 83% (0.2934 g, 0.38 mmol). 1H NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: -15.66, -15.27, 1.46, 1.56, 2.14, 5.91, 17.15, 17.58, 23.56, 24.05, 24.85. HRMS-DART (m/z): $[M-Br]^+$ calc'd for $C_{36}H_{39}N_3O_2BrNi$, 684.32; found, 684.11.

A.5.16 Synthesis of $C_{36}H_{39}N_2Br$ (**L21**)

To MeOH (25 mL) was added 5-bromoacenaphthoquinone (0.5 g, 1.9 mmol), 2,6-diisopropylaniline (0.8 mL, 4.2 mmol), and formic acid (0.3 mL, 7.6 mmol). The reaction was heated at reflux for 24 h, cool to RT, filtered, and washed with MeOH to yield **L21** as a yellow-orange solid. Yield: 45% (0.4904 g, 0.855 mmol). 1H NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 0.97 (d, 12H), 1.23 (d, 12H), 2.99 (m, 4H), 6.44 (d, 1H), 6.67 (d, 1H), 7.28 (s, 6H), 7.46 (t, 1H), 7.61 (d, 1H), 8.09 (d, 1H). ^{13}C NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 23.24, 23.53, 28.79, 123.71, 124.24, 124.66, 128.49, 129.15, 129.22, 129.81, 130.87, 131.53, 135.39, 141.72, 147.40, 160.25, 160.45. HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{36}H_{39}N_2Br$, 579.23; found, 579.19.

A.5.17 Synthesis of $C_{36}H_{39}N_2Br_3Ni$ (**21**)

Under an inert atmosphere, (DME)NiBr₂ (0.133 g, 0.43 mmol) in DCM (5 mL) was added to **L21** (0.25 g, 0.43 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **21**. Yield: 69% (0.2383 g, 0.30 mmol). 1H NMR of (300 MHz, 25 °C, CD_2Cl_2), δ , ppm: -15.79, 1.52, 2.08, 3.37, 5.7, 17.48, 24.06. HRMS-DART (m/z): $[M-Br]^+$ calc'd for $C_{36}H_{39}N_2Br_2Ni$, 718.22; found, 717.02.

A.5.18 Synthesis of 4-bromo-2,6-diisopropylaniline

4-bromo-2,6-diisopropylaniline was synthesized following modified literature procedure.²⁴⁸ Benzyltrimethylammonium tribromide (4.4 g, 11.3 mmol) was dissolved in DCM (20 mL) then added to 2,6-diisopropylaniline (2.1 mL, 11.3 mmol) in DCM (20 mL). The reaction mixture was stirred for 40 minutes then washed with 0.5 M NaOH solution and H₂O. All volatiles were removed under vacuum to yield 4-bromo-2,6-diisopropylaniline as a red oil. Yield: 85% (2.5 g, 9.6 mmol). 1H NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 1.25 (d, 12H), 2.89 (m, 2H), 7.12 (s, 2H). ^{13}C NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 22.35, 28.13, 111.23, 125.86, 134.71, 139.42.

A.5.19 Synthesis of $C_{36}H_{38}N_2Br_2$ (**L22**)

To a round bottom flask equipped with a Soxhlet and condenser was added acenaphthoquinone (0.5 g, 2.7 mmol), 4-bromo-2,6-diisopropylaniline (1.55 g, 6.0 mmol), *p*-toluene sulfonic acid (0.026 g, 0.135 mmol), and dry toluene (16 mL). The reaction was allowed to reflux for 2 days, cool to RT, and then all volatiles were removed under reduced pressure. The resulting yellow solid was washed with Et₂O to yield **L22**. Yield: 68% (1.2088 g, 1.8 mmol). 1H NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 0.95 (d, 12H), 1.22 (d, 12H), 2.96 (m, 4H), 6.78 (d, 2H), 7.38-7.46 (m, 6H), 7.93 (d, 2H). ^{13}C NMR of (300 MHz, 25 °C, $CDCl_3$), δ , ppm: 23.00, 23.32, 28.91, 117.89, 123.58, 126.96, 128.17, 129.22, 129.52, 131.33, 138.01, 141.26, 146.38, 161.36. HRMS-DART (m/z): $[M+H]^+$ calc'd for $C_{36}H_{38}N_2Br_2$, 659.14; found, 659.10.

A.5.20 Synthesis of $C_{36}H_{38}N_2Br_4Ni$ (**22**)

Under an inert atmosphere, (DME)NiBr₂ (0.117 g, 0.37 mmol) in DCM (5 mL) was added to **L22** (0.25 g, 0.37 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **22**. Yield: 87%

(0.2816 g, 0.32 mmol). ^1H NMR of (300 MHz, 25 °C, CD_2Cl_2), δ , ppm: 1.27, 1.53, 2.04, 5.84, 17.28, 23.63, 24.12. HRMS-DART (m/z): $[\text{M}-\text{Br}]^+$ calc'd for $\text{C}_{36}\text{H}_{38}\text{N}_2\text{Br}_3\text{Ni}$, 797.12; found, 796.91.

A.5.21 Synthesis of $\text{C}_{36}\text{H}_{38}\text{N}_2\text{Cl}_2$ (**L23**)

To a round bottom flask equipped with a Soxhlet and condenser was added acenaphthoquinone (0.248 g, 1.36 mmol), 4-chloro-2,6-diisopropylaniline (0.6338 g, 3.0 mmol), *p*-toluene sulfonic acid (0.013 g, 0.068 mmol), and dry toluene (16 mL). The reaction was allowed to reflux for 2 days, cool to RT, and then all volatiles were removed under reduced pressure. The resulting yellow-orange solid was washed with Et_2O to yield **L23**. Yield: 74% (0.575 g, 1.0 mmol). ^1H NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 0.97 (d, 12H), 1.23 (d, 12H), 2.99 (m, 4H), 6.80 (d, 2H), 7.28 (s, 4H), 7.45 (t, 2H), 7.95 (d, 2H). ^{13}C NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 22.99, 23.31, 28.92, 123.56, 124.04, 128.16, 129.26, 129.50, 129.91, 131.34, 137.65, 141.19, 145.89, 161.50. HRMS-DART (m/z): $[\text{M}+\text{H}]^+$ calc'd for $\text{C}_{36}\text{H}_{38}\text{N}_2\text{Cl}_2$, 569.24; found, 569.21.

A.5.22 Synthesis of $\text{C}_{36}\text{H}_{38}\text{N}_2\text{Cl}_2\text{Br}_2\text{Ni}$ (**23**)

Under an inert atmosphere, (DME)NiBr₂ (0.135 g, 0.44 mmol) in DCM (5 mL) was added to **L23** (0.25 g, 0.44 mmol) in DCM (10 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **23**. Yield: 68% (0.2376 g, 0.3 mmol). ^1H NMR of (300 MHz, 25 °C, CD_2Cl_2), δ , ppm: 1.51, 2.03, 3.34, 3.50, 5.83, 17.28, 17.30, 23.71, 23.92. HRMS-DART (m/z): $[\text{M}-\text{Br}]^+$ calc'd for $\text{C}_{36}\text{H}_{38}\text{N}_2\text{Cl}_2\text{BrNi}$, 708.21; found, 707.03.

A.5.23 Synthesis of 2,6-diisopropyl-4-methylaniline

To a Schlenk flask was added 4-bromo-2,6-di-2-propyl-*N,N*-bis-trimethylsilylaminile (4.5 g, 11.2 mmol) and Et_2O (40 mL), then cooled to -78 °C. *n*-BuLi (2.3 M, 5.4 mL, 12.4 mmol) was added dropwise then the reaction was allowed to warm to RT and stir for 2 h. The reaction was cooled to -78 °C and MeI (0.84 mL, 13.4 mmol) was added dropwise before allowing to warm to RT and stir for 2 h. the reaction was quenched with H_2O at 0 °C, extracted, washed with brine, dried with NaSO_4 , and all volatiles were removed under vacuum to yield a red oil. The desilylation was accomplished by stirring the resultant red oil in dry THF (10 mL) with TBAF (1 M, 24.5 mL, 22.6 mmol) overnight. To the mixture was add of H_2O , extracted with DCM, washed with brine dried with NaSO_4 , and all volatiles were removed under vacuum. The crude product was purified via silica gel flash column chromatography using hexanes:DCM as an eluent to yield 2,6-diisopropyl-4-methylaniline as a red oil. Yield: 28% (0.5902 g, 3.1 mmol). ^1H NMR (300 MHz, 25 °C, CDCl_3), δ , ppm: 1.39 (d, 12H), 2.40 (s, 3H), 3.03 (m, 2H), 3.68 (br, 2H), 6.98 (s, 2H). ^{13}C NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 21.11, 21.14, 22.62, 27.97, 123.50, 127.48, 132.71, 137.73. HRMS-DART (m/z): $[\text{M}+\text{H}]^+$ calc'd for $\text{C}_{13}\text{H}_{21}\text{N}$, 192.17; found, 192.16.

A.5.24 Synthesis of $\text{C}_{38}\text{H}_{44}\text{N}_2$ (**L24**)

To a round bottom flask equipped with a Soxhlet and condenser was added acenaphthoquinone (0.255 g, 1.4 mmol), 2,6-diisopropyl-4-methylaniline (0.59 g, 3.1 mmol), *p*-toluene sulfonic acid (0.013 g, 0.07 mmol), and dry toluene (16 mL). The reaction was allowed to reflux for 2 days, cool to RT, and then all volatiles were removed under reduced pressure. The resulting orange solid was washed with Et_2O to yield **L24**. Yield: 60% (0.4432 g, 0.8 mmol). ^1H NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 0.99 (d, 12H), 1.25 (d, 12H), 2.48 (s, 6H), 3.03 (m, 4H),

6.72 (d, 2H), 7.10 (s, 4H), 7.40 (t, 2H), 7.89 (d, 2H). ^{13}C NMR of (300 MHz, 25 °C, CDCl_3), δ , ppm: 21.68, 23.31, 23.54, 28.62, 123.44, 124.28, 127.92, 128.82, 129.75, 131.20, 133.39, 135.33, 140.79, 145.19, 161.36. HRMS-DART (m/z): $[\text{M}+\text{H}]^+$ calc'd for $\text{C}_{38}\text{H}_{44}\text{N}_2$, 529.35; found, 529.31.

A.5.25 Synthesis of $\text{C}_{38}\text{H}_{44}\text{N}_2\text{Br}_2\text{Ni}$ (**24**)

Under an inert atmosphere, $(\text{DME})\text{NiBr}_2$ (0.256 g, 0.8 mmol) in DCM (5 mL) was added to **L24** (0.44 g, 0.8 mmol) in DCM (15 mL). The reaction was allowed to stir overnight and then all volatiles were removed under reduced pressure. The resulting red solid was washed with cold hexanes to yield complex **24**. Yield: 68% (0.3525 g, 0.47 mmol). ^1H NMR of (300 MHz, 25 °C, CD_2Cl_2), δ , ppm: 0.97, 1.19, 1.50, 1.97, 2.44, 2.93, 5.77, 6.72, 7.10, 7.38, 7.89, 17.19, 23.85, 24.37. HRMS-DART (m/z): $[\text{M}-\text{Br}]^+$ calc'd for $\text{C}_{38}\text{H}_{44}\text{N}_2\text{BrNi}$, 667.38; found, 667.14.

A.5.26 General Ethylene Polymerization Procedure

To a Fisher-Porter bottle was added PMAO-IP (53.4 mg, 0.92 mmol), toluene (148 mL), and a magnetic stir bar. The bottle was sealed and placed in a room temperature water bath. The vessel was pressurized with ethylene (15 psi) and allowed to equilibrate under constant pressure for 10 min with stirring. Catalyst (10 μmol) in DCM (2 mL) was injected to initiate polymerization, and was stirred continuously for 30 min. The polymerization was quenched via addition of MeOH (10 mL), and the polymer was precipitated by adding excess acidic MeOH (5% HCl in MeOH), then dried in a vacuum oven at 70 °C overnight.

A.6 Supporting Information – Chapter 5

A.6.1 NMR Spectroscopy

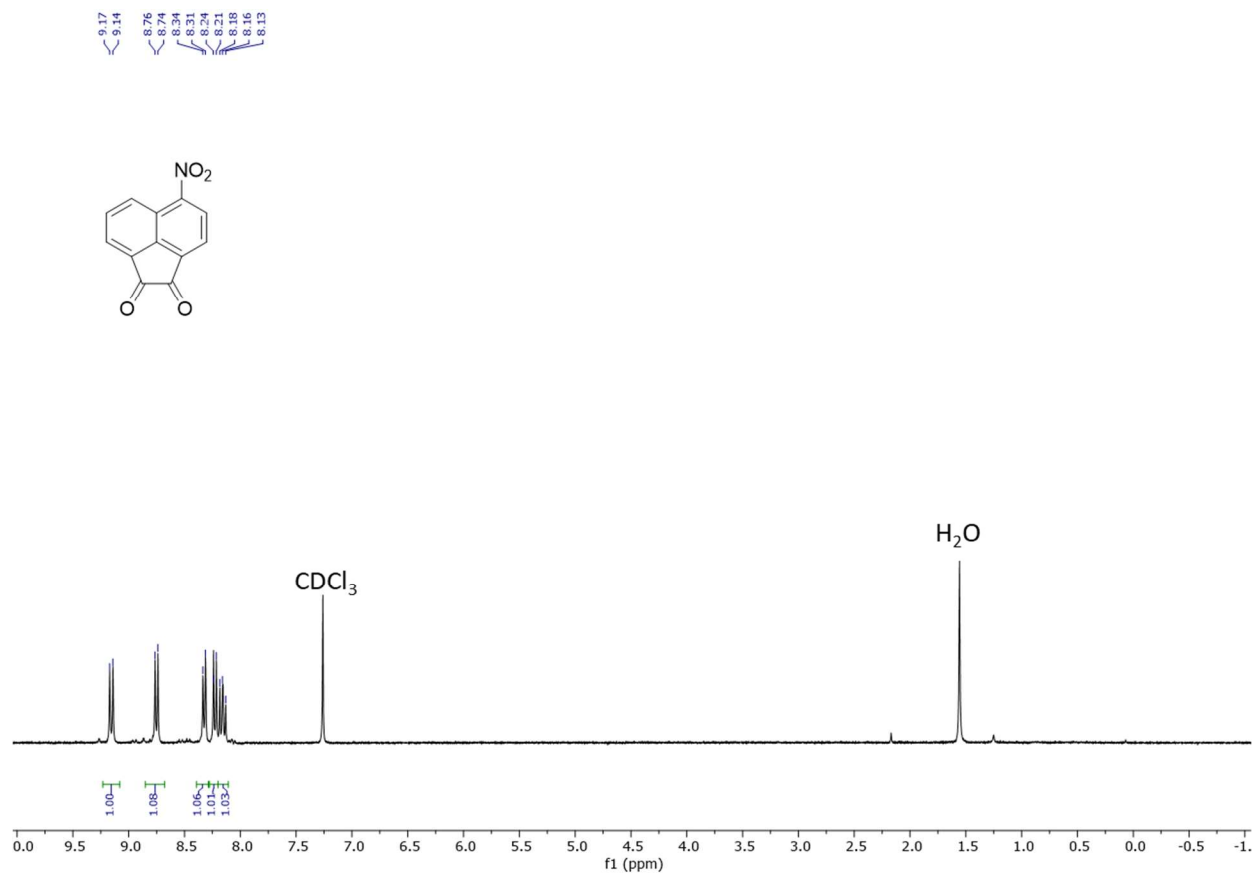


Figure A.87 ¹H NMR (300 MHz, 25 °C, CDCl₃) of 5-NO₂ ANQ, δ , ppm: 8.16 (t, 1H, aromatic), 8.23 (d, 1H, aromatic), 8.33 (d, 1H, aromatic), 8.75 (d, 1H, aromatic), 9.15 (d, 1H, aromatic).

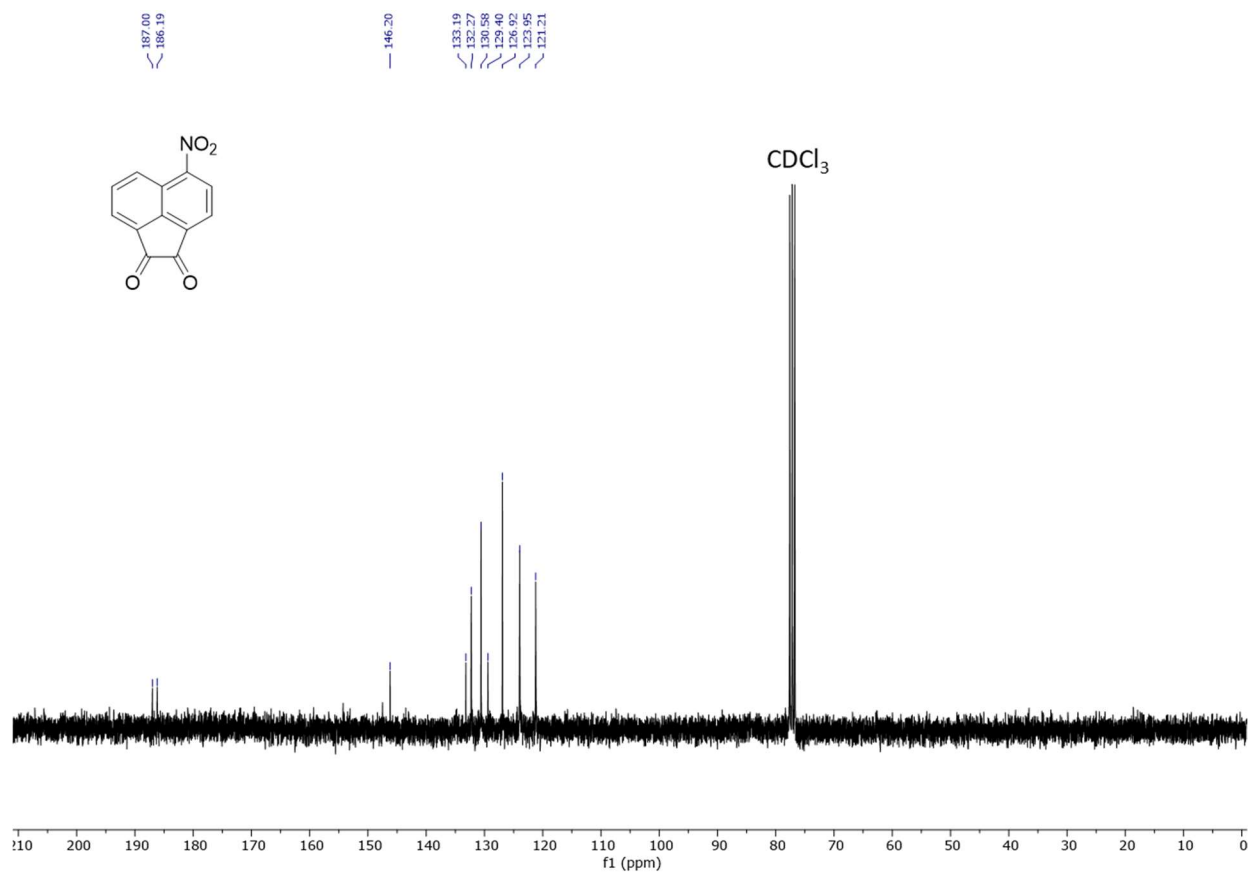


Figure A.88 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of **5-NO₂ ANQ**, δ, ppm: 121.21 (aromatic), 123.95 (aromatic), 126.92 (aromatic), 129.40 (aromatic), 130.58 (aromatic), 132.27 (aromatic), 133.19 (aromatic), 146.20 (aromatic-NO₂), 186.19 (C=O), 187.00 (C=O).

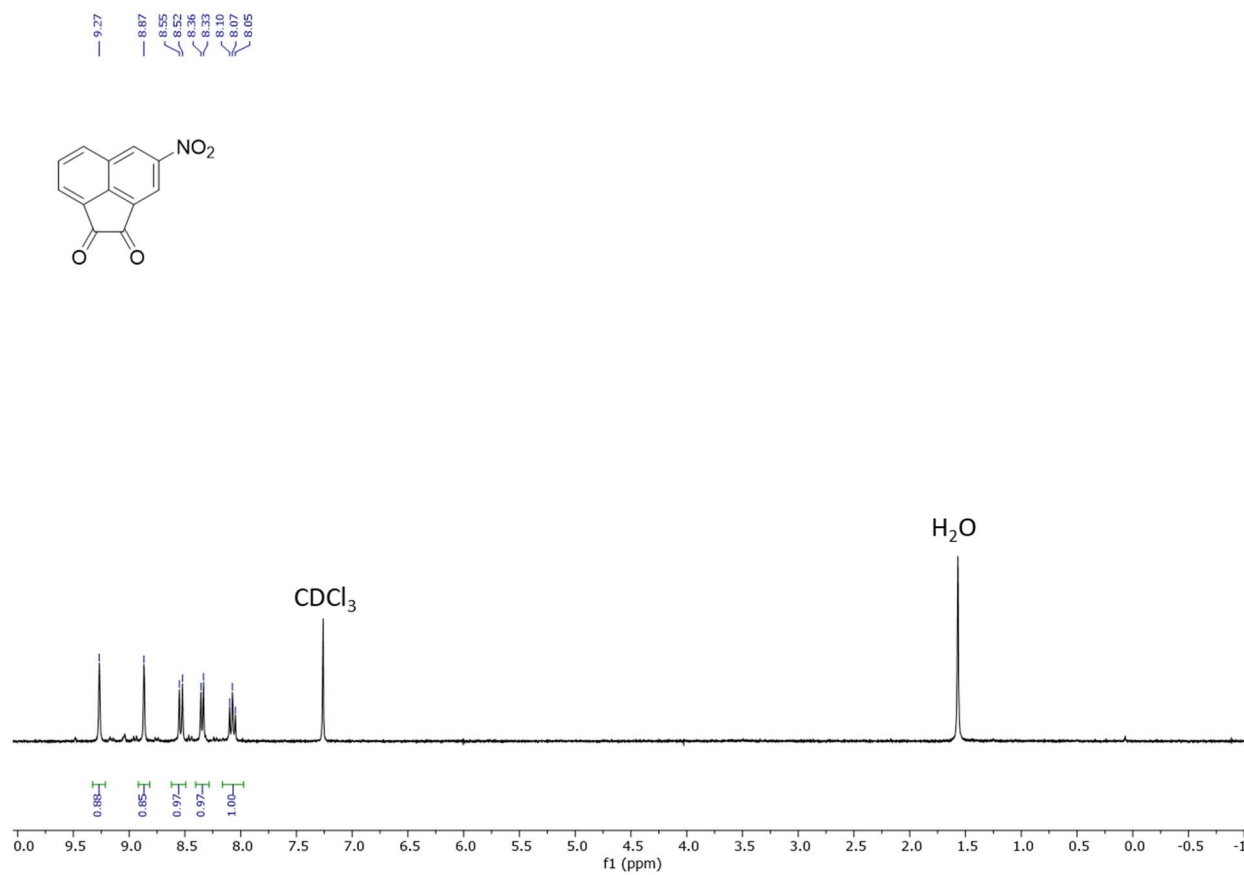


Figure A.89 ¹H NMR (300 MHz, 25 °C, CDCl₃) of **4-NO₂ ANQ**, δ, ppm: 8.07 (t, 1H, aromatic), 8.35 (d, 1H, aromatic), 8.54 (d, 1H, aromatic), 8.87 (s, 1H, aromatic), 9.27 (s, 1H, aromatic).

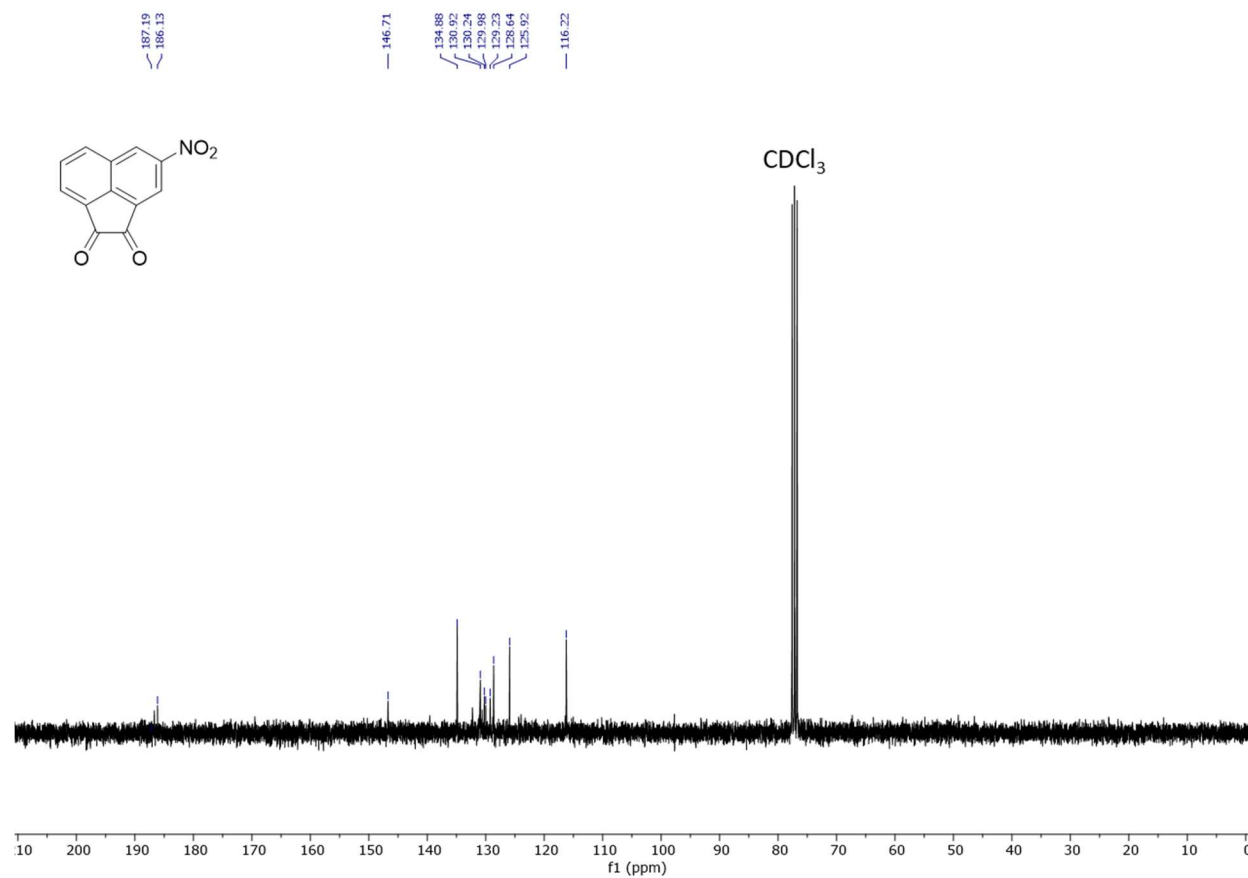


Figure A.90 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of **4-NO₂ ANQ**, δ, ppm: 116.22 (aromatic), 125.92 (aromatic), 128.64 (aromatic), 129.23 (aromatic), 129.98 (aromatic), 130.24 (aromatic), 130.92 (aromatic), 132.32 (aromatic), 134.88 (aromatic), 146.71 (aromatic-NO₂), 186.13 (C=O), 187.19 (C=O).

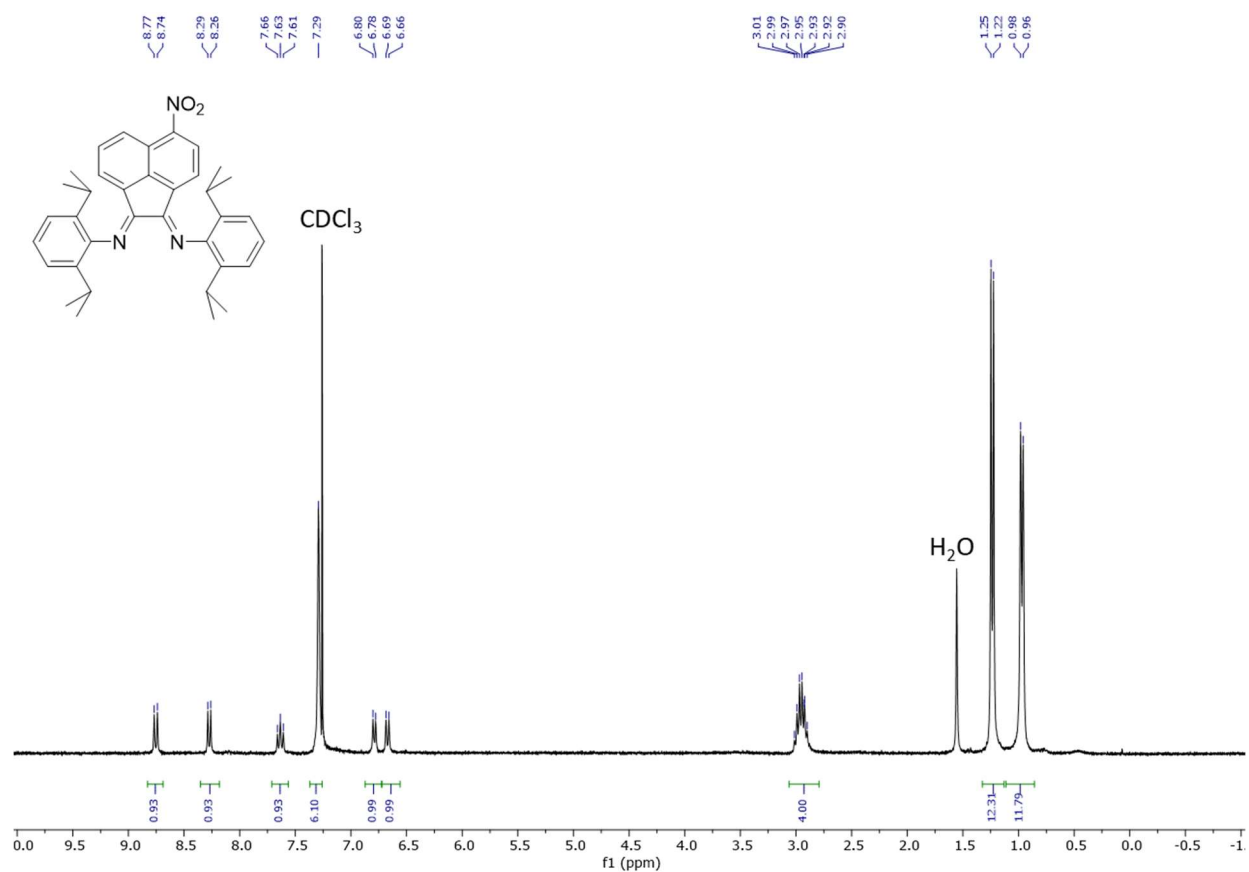


Figure A.91 ^1H NMR (300 MHz, 25°C , CDCl_3) of **L14**, δ , ppm: 0.97 (d, 12H, CH_3), 1.24 (d, 12H, CH_3), 2.95 (m, 4H, CH), 6.68 (d, 1H, aromatic), 6.79 (d, 1H, aromatic), 7.29 (s, 6H, aromatic), 7.63 (t, 1H, aromatic), 8.28 (d, 1H, aromatic), 8.76 (d, 1H, aromatic).

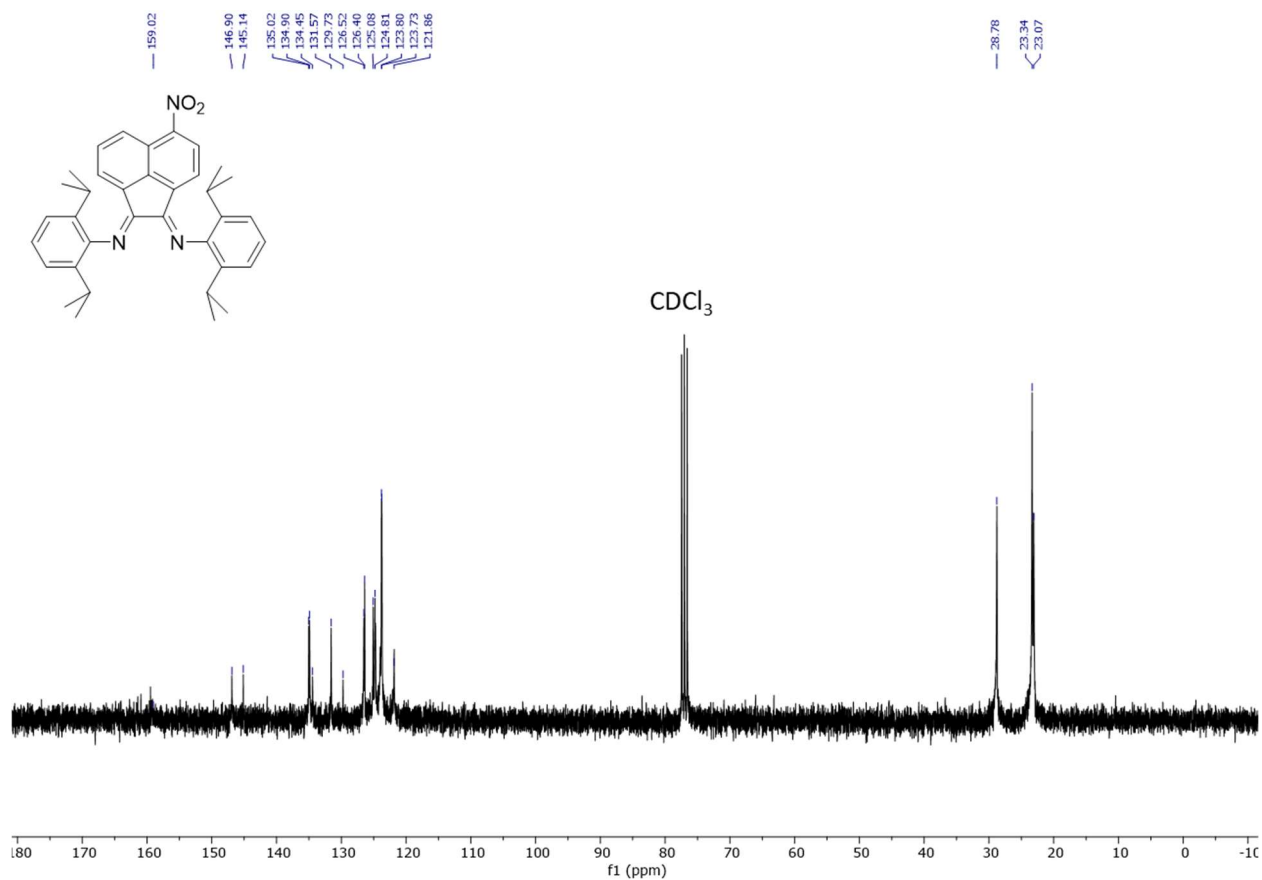


Figure A.92 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of **L14**, δ , ppm: 23.07 (CH_3), 23.34 (CH_3), 28.78 (CH), 121.86 (aromatic), 123.73 (aromatic), 123.80 (aromatic), 124.81 (aromatic), 125.08 (aromatic), 126.40 (aromatic), 126.52 (aromatic), 129.73 (aromatic), 131.57 (aromatic), 134.45 (aromatic), 134.90 (aromatic), 135.02 (aromatic), 145.14 (aromatic), 146.90 (aromatic), 159.02 ($\text{C}=\text{N}$).

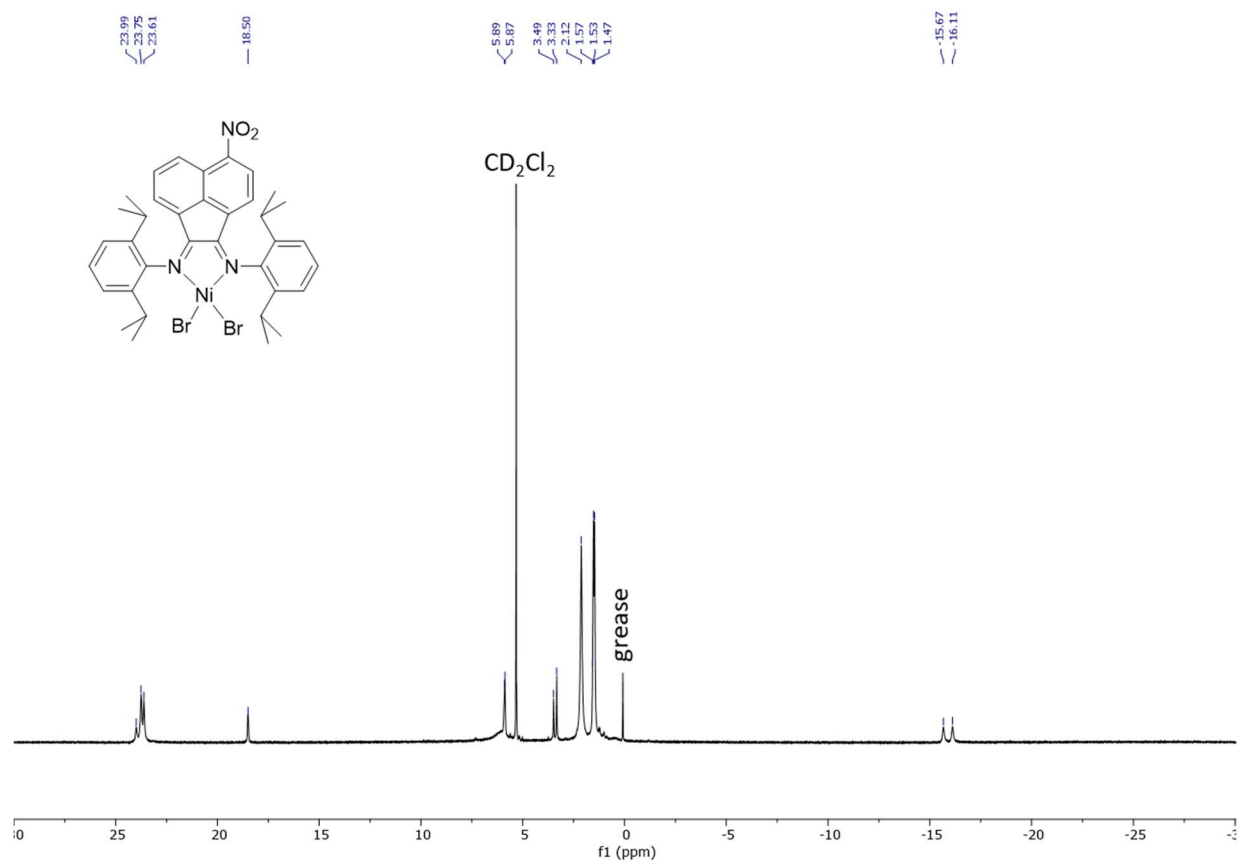


Figure A.93 ^1H NMR (300 MHz, 25 °C, CD_2Cl_2) of **14**, δ , ppm: -16.11, -15.67, 1.53, 2.12, 3.33, 3.49, 5.88, 18.50, 23.75.

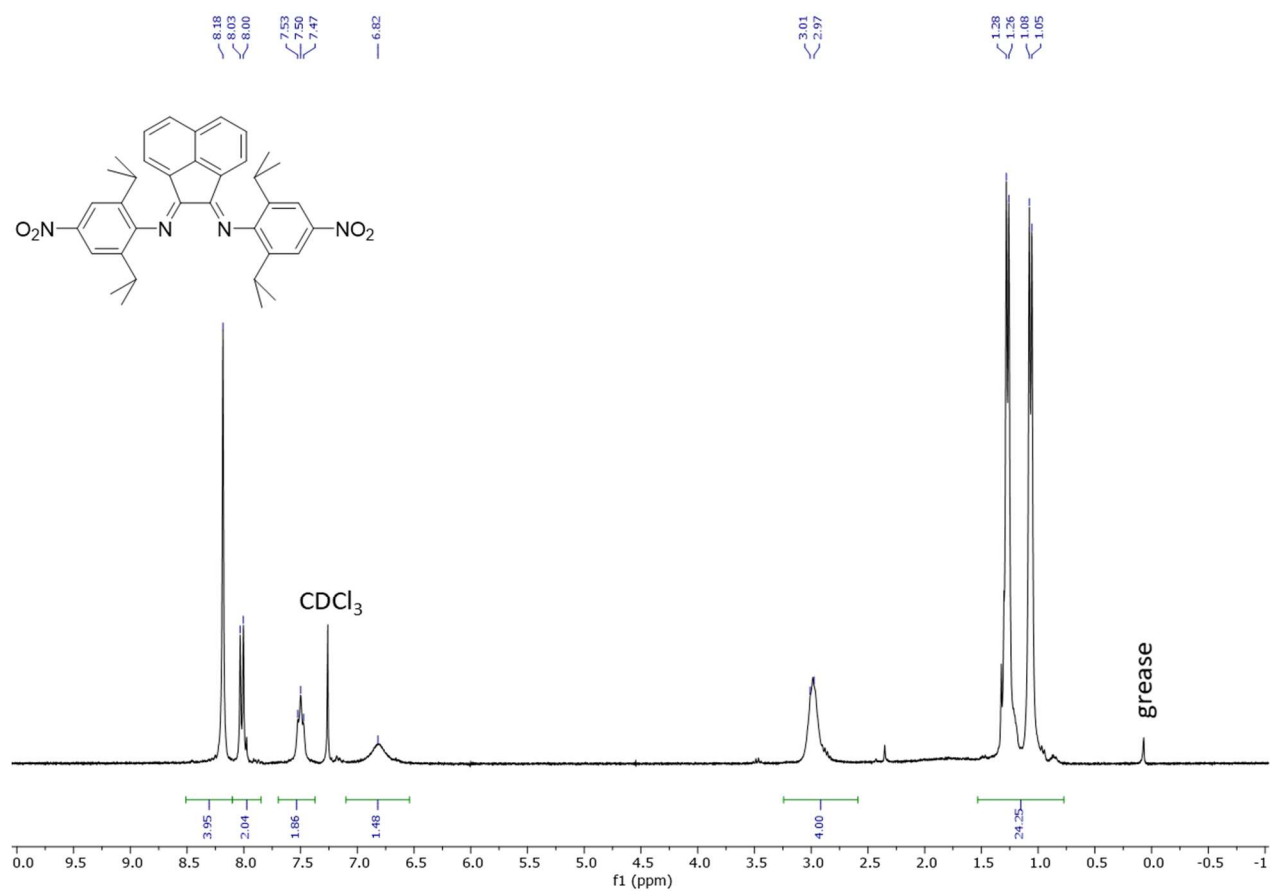


Figure A.94 ^1H NMR (300 MHz, 25 °C, CDCl_3) of **L15**, δ , ppm: 1.06 (d, 12H, CH_3), 1.27 (d, 12H, CH_3), 2.99 (br, 4H, CH), 6.82 (br, 2H, aromatic), 7.5 (t, 2H, aromatic), 8.01 (d, 2H, aromatic), 8.18 (s, 4H, aromatic).

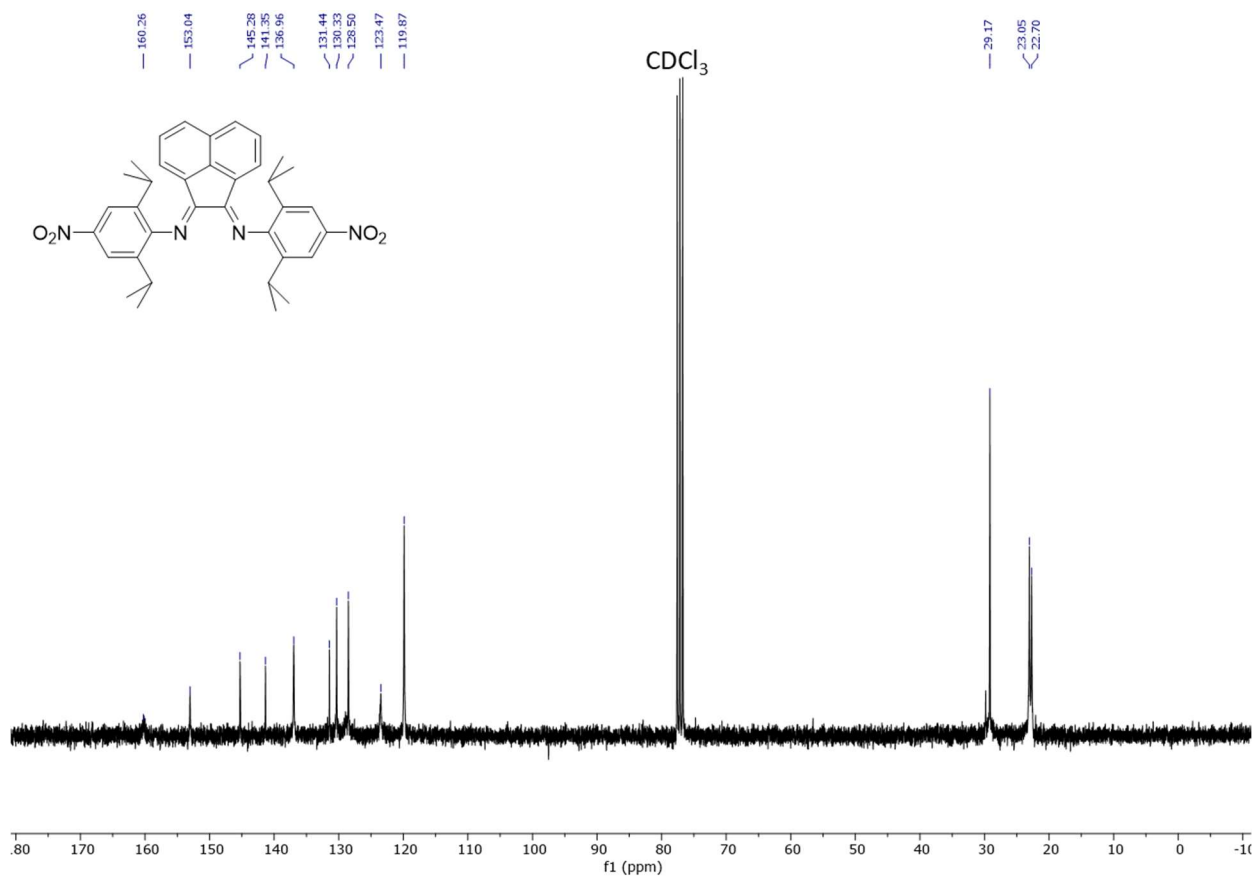


Figure A.95 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of **L15**, δ, ppm: 22.70 (CH₃), 23.05 (CH₃), 29.17 (CH), 119.87 (aromatic), 123.47 (aromatic), 128.50 (aromatic), 130.33 (aromatic), 131.44 (aromatic), 136.96 (aromatic), 141.35 (aromatic), 145.28 (aromatic), 153.04 (aromatic), 160.26 (C=N).

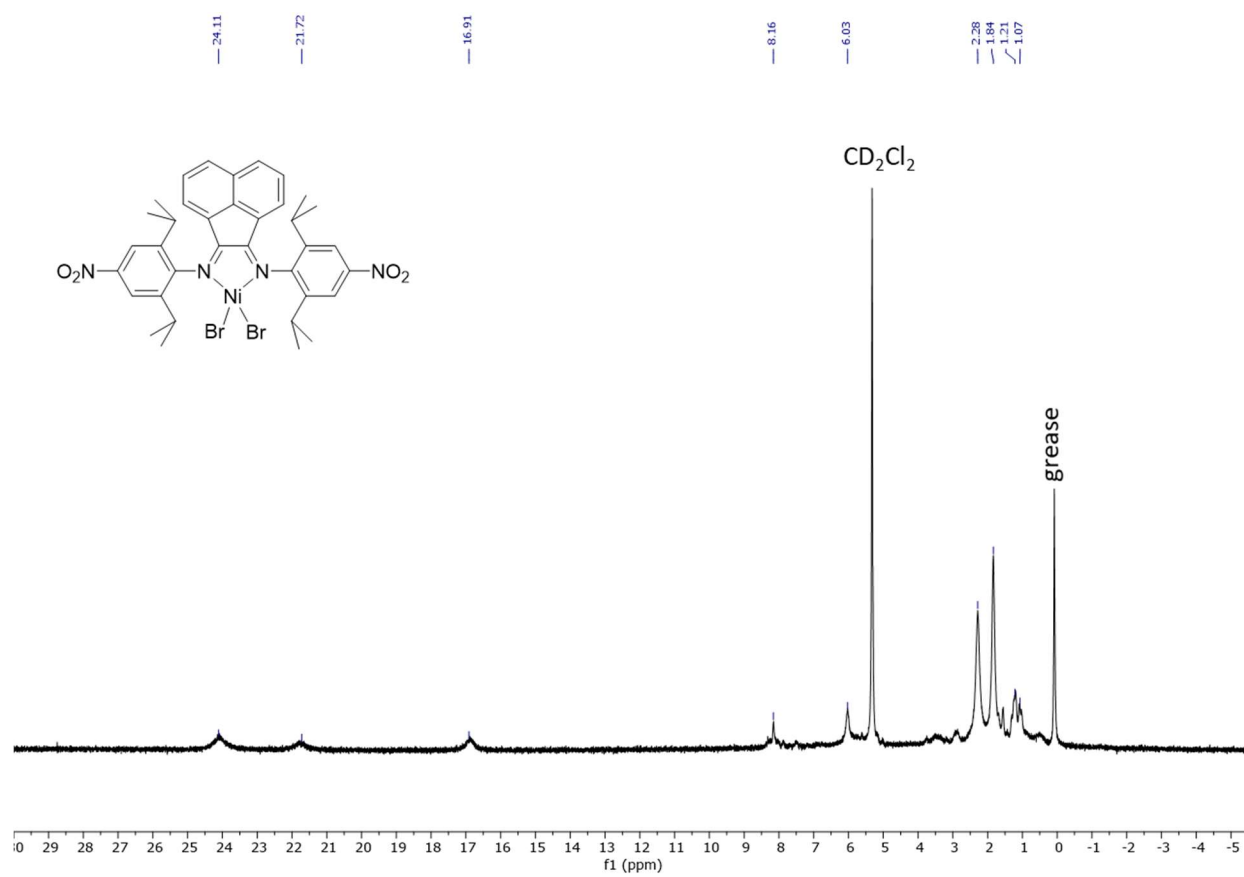


Figure A.96 ^1H NMR (300 MHz, 25°C , CD_2Cl_2) of **15**, δ , ppm: 1.07, 1.21, 1.84, 2.28, 6.03, 8.16, 16.91, 21.72, 24.11.

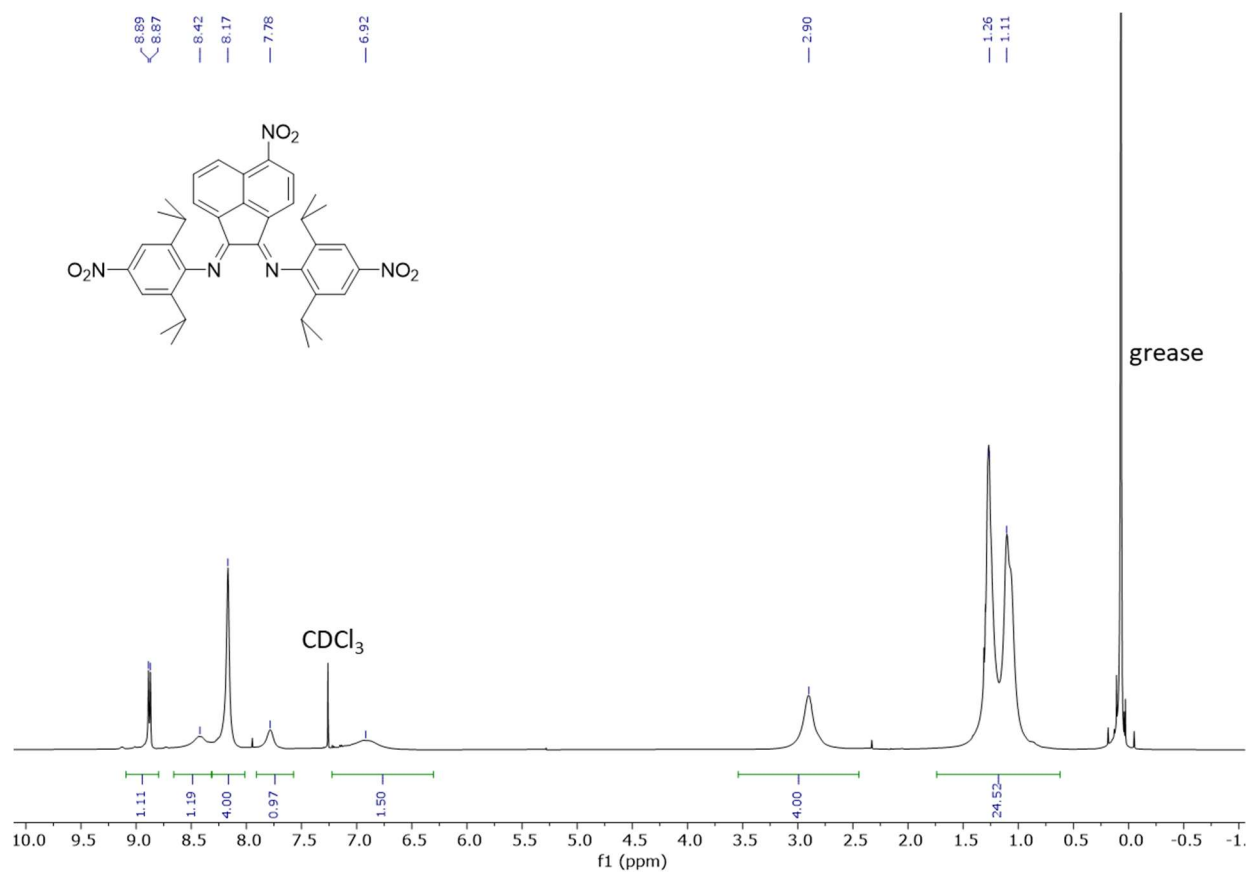


Figure A.97 ^1H NMR (300 MHz, 25°C , CDCl_3) of **L16**, δ , ppm: 1.11 (s, 12H, (CH_3)), 1.26 (s, 12H, (CH_3)), 2.90 (s, 4H, (CH)), 6.92 (br, 2H, aromatic), 7.78 (br, 1H, aromatic), 8.17 (s, 4H, aromatic), 8.42 (br, 1H, aromatic), 8.88 (d, 1H, aromatic).

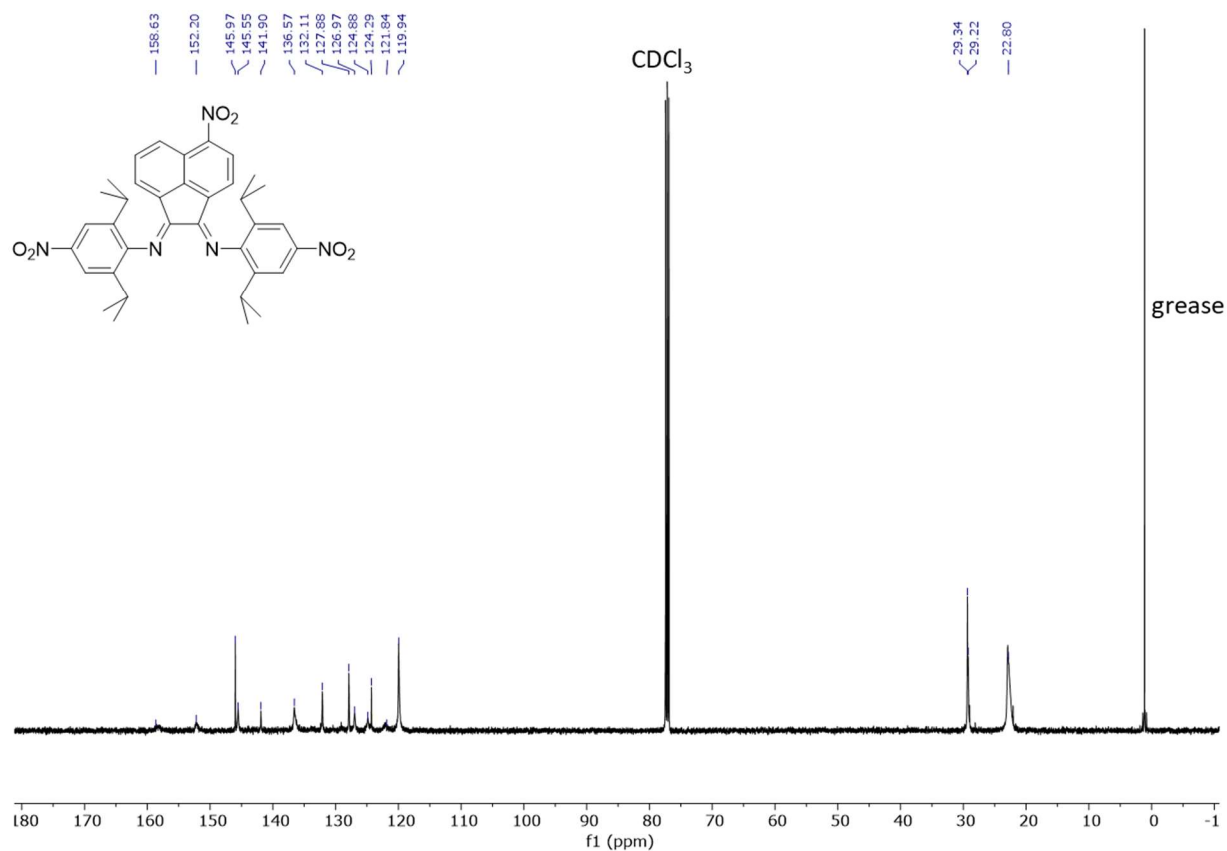


Figure A.98 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of **L16**, δ , ppm: 22.80 (CH_3), 22.92 (CH_3), 29.22 (CH), 29.34 (CH), 119.94 (aromatic), 121.84 (aromatic), 124.29 (aromatic), 124.88 (aromatic), 126.97 (aromatic), 127.88 (aromatic), 132.11 (aromatic), 136.57 (aromatic), 141.90 (aromatic), 145.55 (aromatic), 145.97 (aromatic), 152.20 (aromatic), 158.63 (C=N).

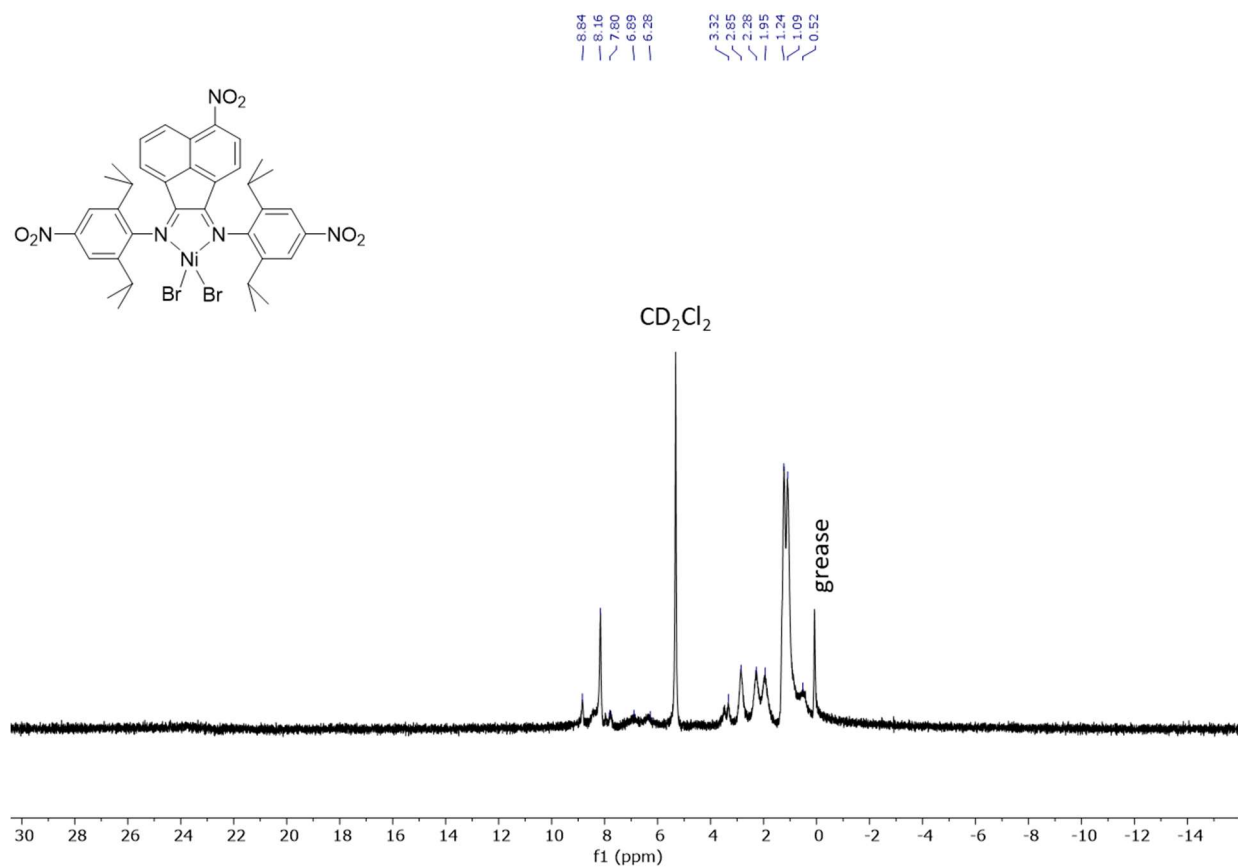


Figure A.99 ^1H NMR (300 MHz, 25 °C, CD_2Cl_2) of **16**, δ , ppm: 0.52, 1.09, 1.24, 1.95, 2.28, 2.85, 3.32, 6.28, 6.89, 7.80, 8.16, 8.84.

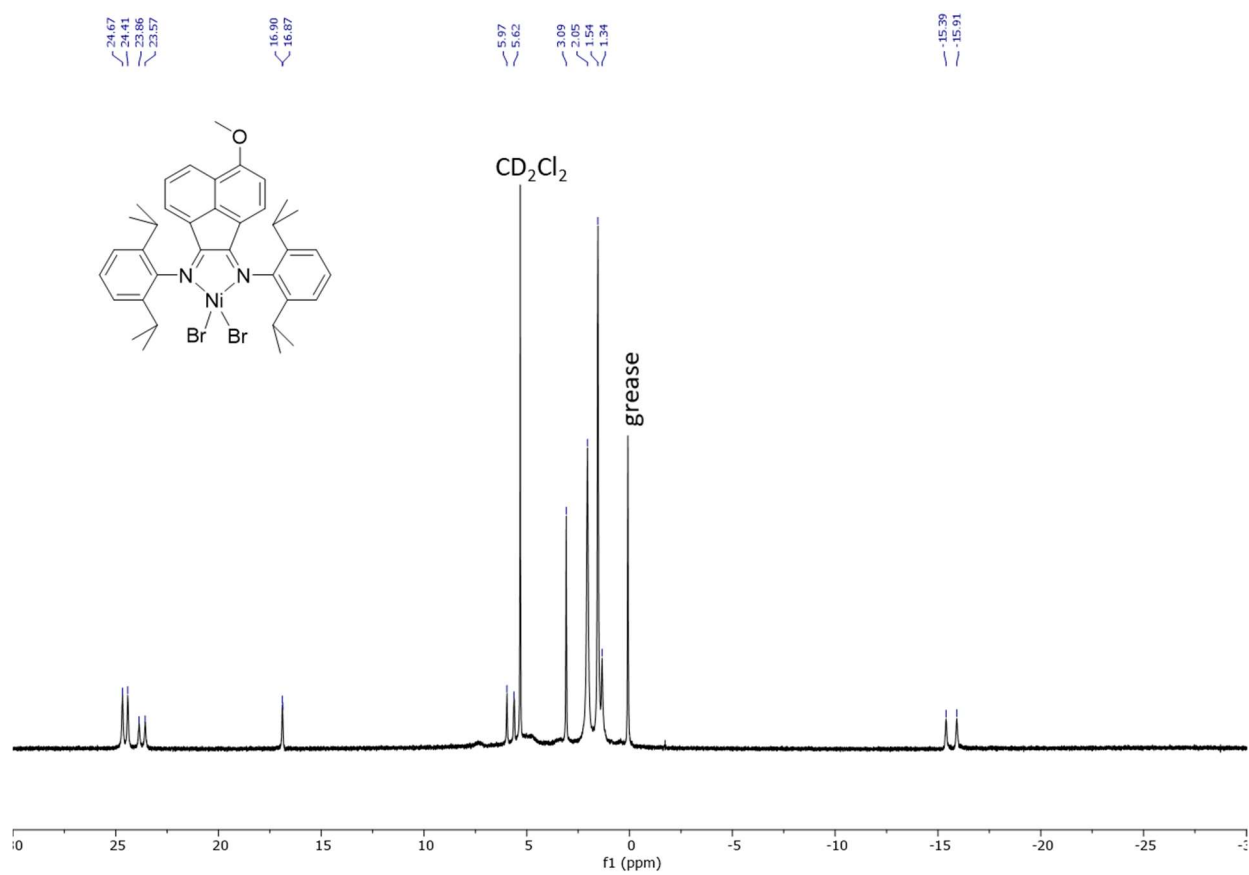


Figure A.100 ^1H NMR (300 MHz, 25 °C, CD_2Cl_2) of 17, δ , ppm: -15.91, -15.39, 1.34, 1.54, 2.05, 3.09, 5.62, 5.97, 16.89, 23.57, 23.86, 24.41, 24.67.

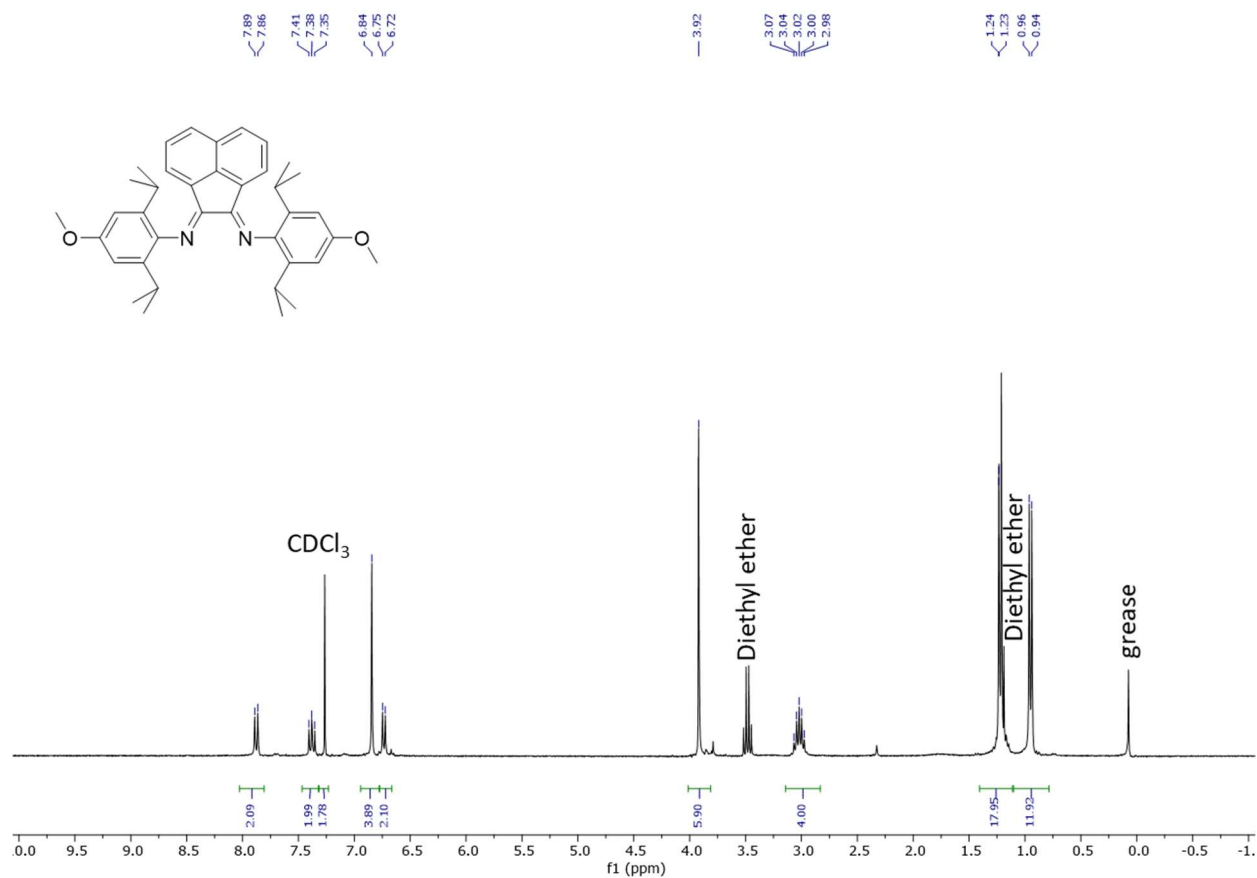


Figure A.101 ^1H NMR (300 MHz, 25°C , CDCl_3) of **L18**, δ , ppm: 0.95 (d, 12H, CH_3), 1.24 (d, 12H, CH_3), 3.02 (m, 4H, CH), 3.92 (s, 6H, CH_3), 6.74 (d, 2H, aromatic), 6.84 (s, 4H, aromatic), 7.38 (t, 2H, aromatic), 7.88 (d, 2H, aromatic).

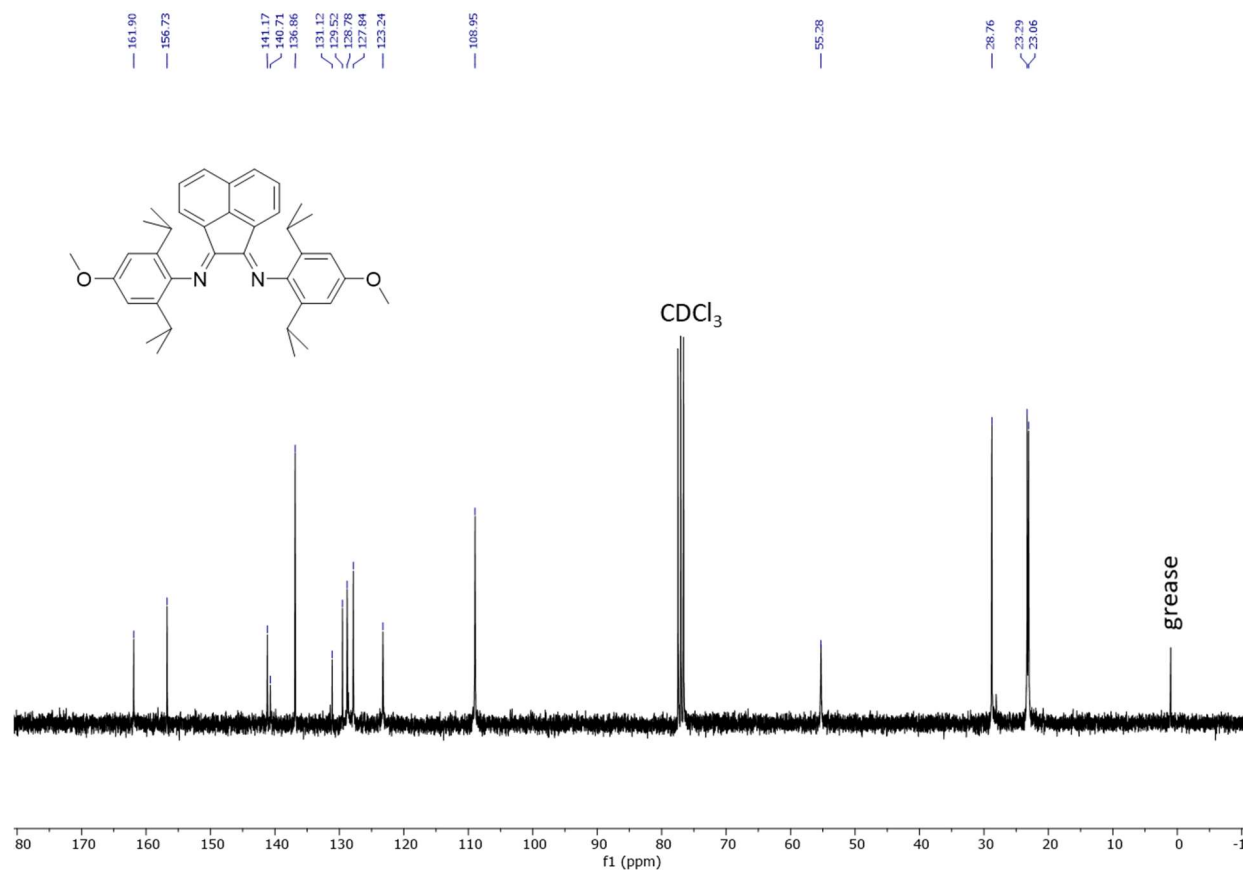


Figure A.102 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of **L18**, δ , ppm: 23.06 (CH₃), 23.29 (CH₃), 28.76 (CH), 55.28 (CH₃), 108.95 (aromatic), 123.24 (aromatic), 127.84 (aromatic), 128.78 (aromatic), 129.52 (aromatic), 131.12 (aromatic), 136.86 (aromatic), 140.71 (aromatic), 141.17 (aromatic), 156.73 (aromatic), 161.90 (C=N).

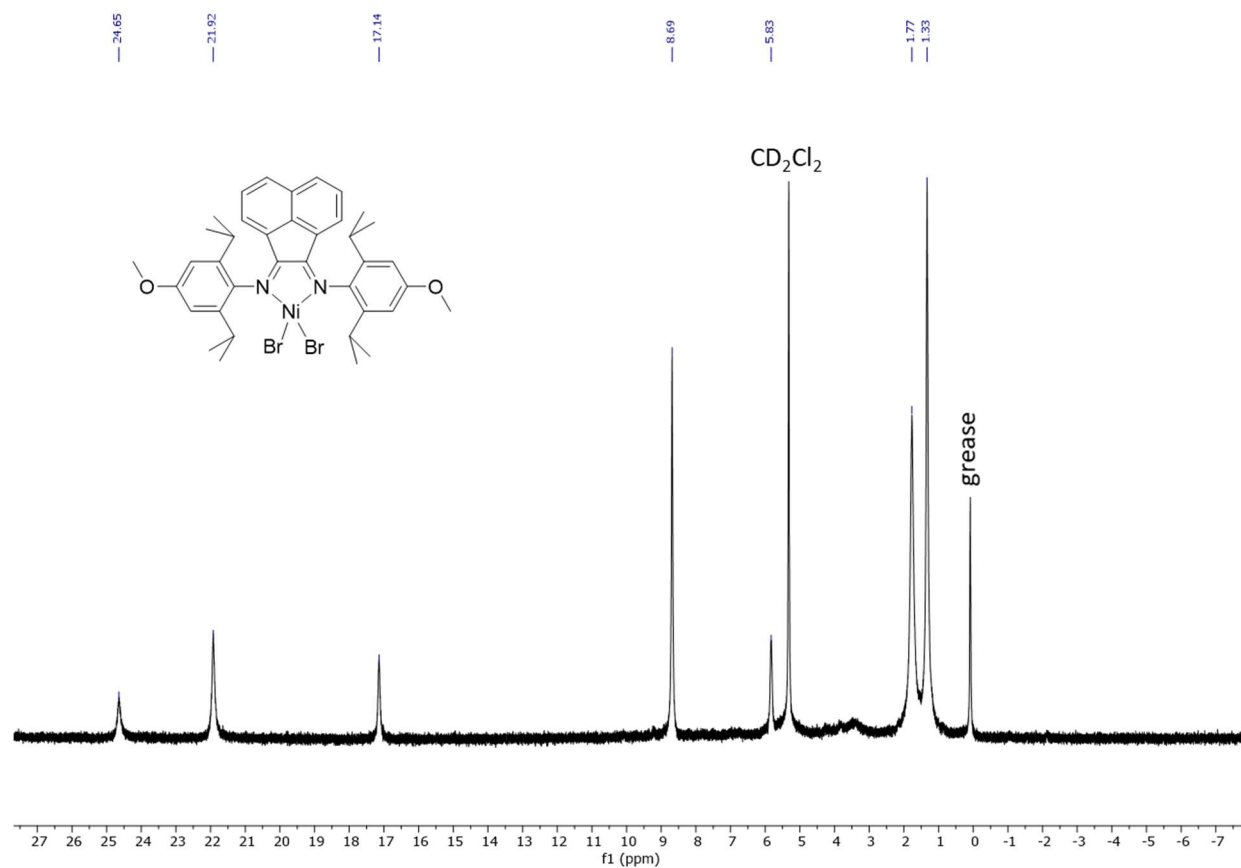


Figure A.103 ^1H NMR (300 MHz, 25 °C, CD_2Cl_2) of **18**, δ , ppm: 1.33, 1.77, 5.83, 8.69, 17.14, 21.92, 24.65.

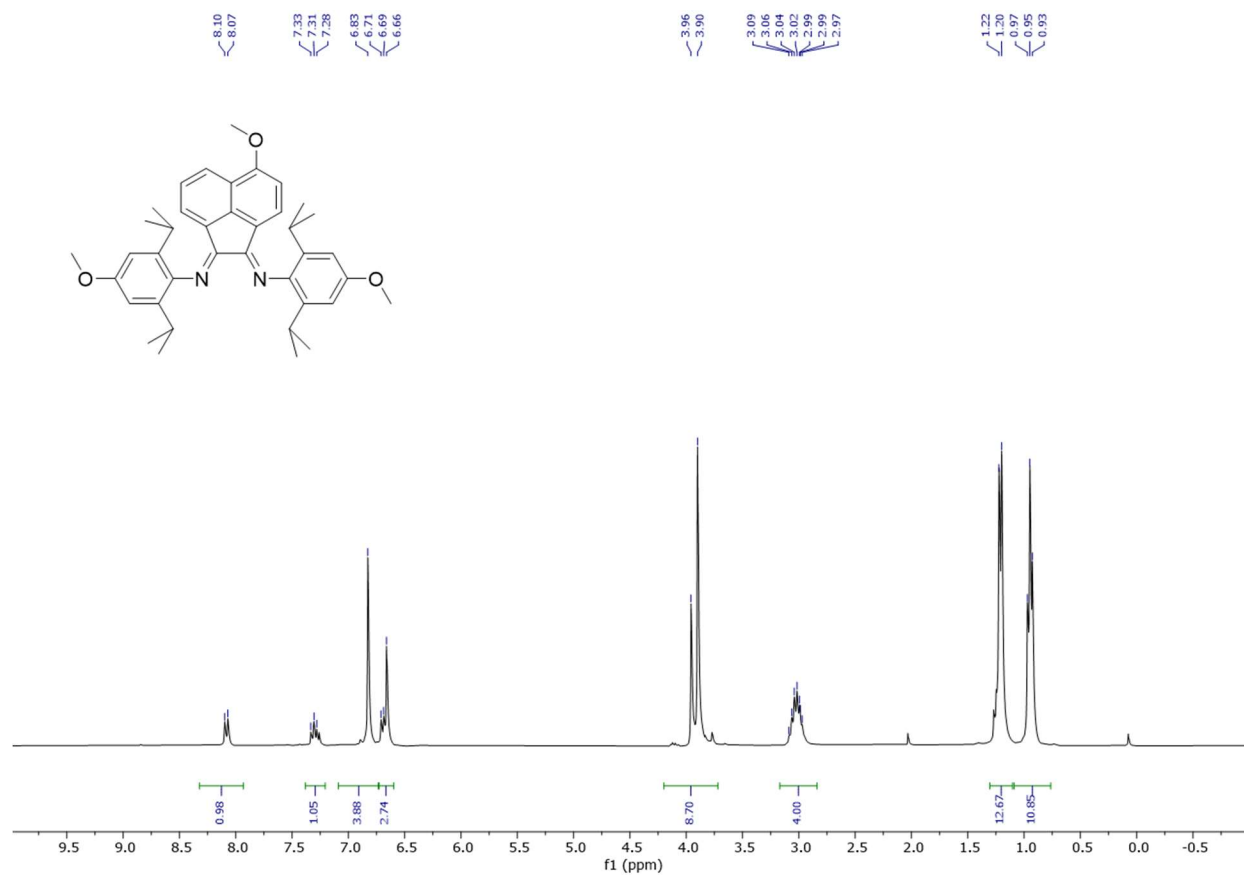


Figure A.104 ^1H NMR (300 MHz, 25 °C, CDCl_3) of **L19**, δ , ppm: 0.95 (t, 12H, CH_3), 1.21 (d, 12H, CH_3), 3.02 (m, 4H, CH), 3.90 (s, 6H, CH_3), 3.96 (s, 3H, CH_3), 6.70 (m, 3H, aromatic), 6.83 (s, 4H, aromatic), 7.31 (t, 1H, aromatic), 8.08 (d, 1H, aromatic).

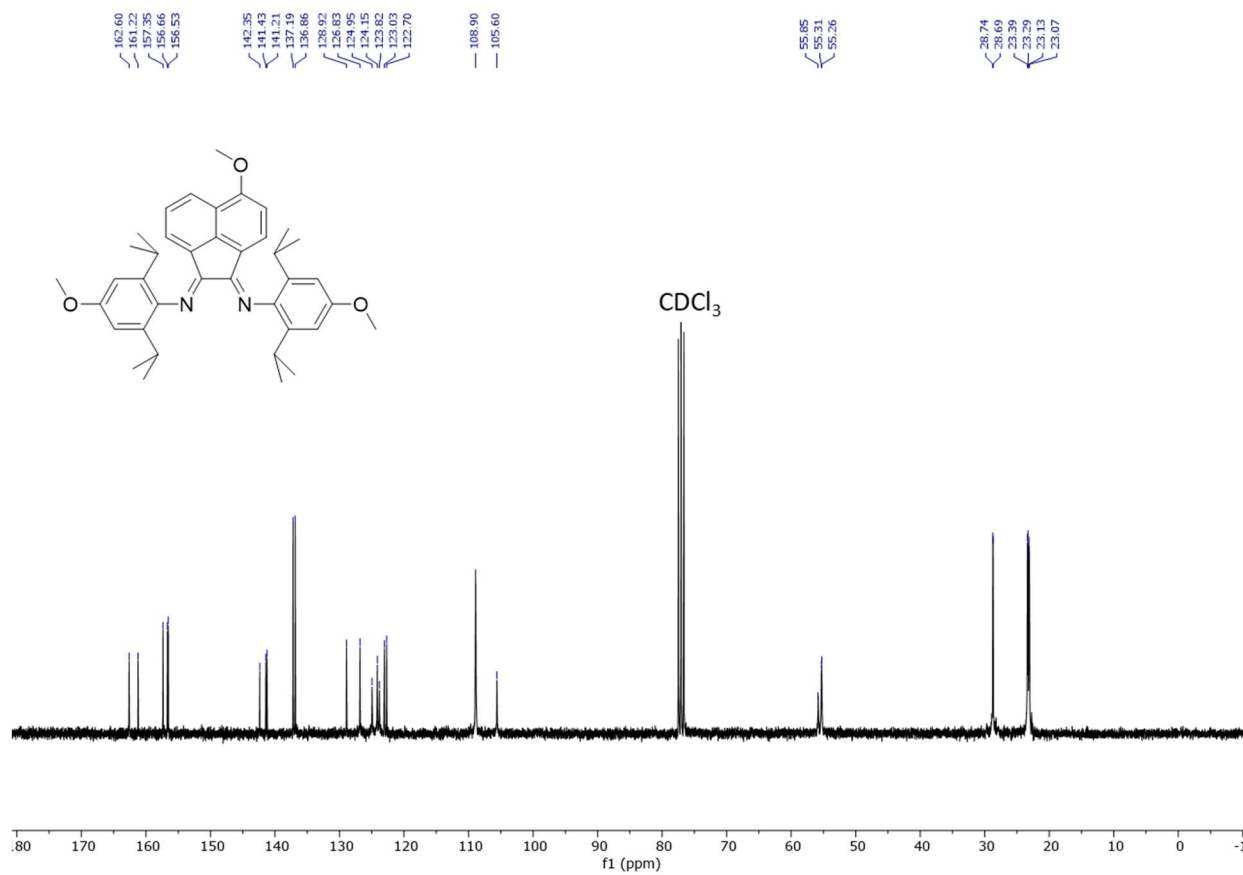


Figure A.105 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of **L19**, δ, ppm: 23.07 (CH₃), 23.13 (CH₃), 23.29 (CH₃), 23.39 (CH₃), 28.69 (CH), 28.74 (CH), 55.26 (CH₃), 55.31 (CH₃), 55.85 (CH₃), 105.60 (aromatic), 108.90 (aromatic), 122.70 (aromatic), 123.03 (aromatic), 123.82 (aromatic), 124.15 (aromatic), 124.95 (aromatic), 126.83 (aromatic), 128.92 (aromatic), 136.86 (aromatic), 137.19 (aromatic), 141.21 (aromatic), 141.43 (aromatic), 142.35 (aromatic), 156.53 (aromatic), 156.66 (aromatic), 157.35 (aromatic), 161.22 (C=N), 162.60 (C=N).

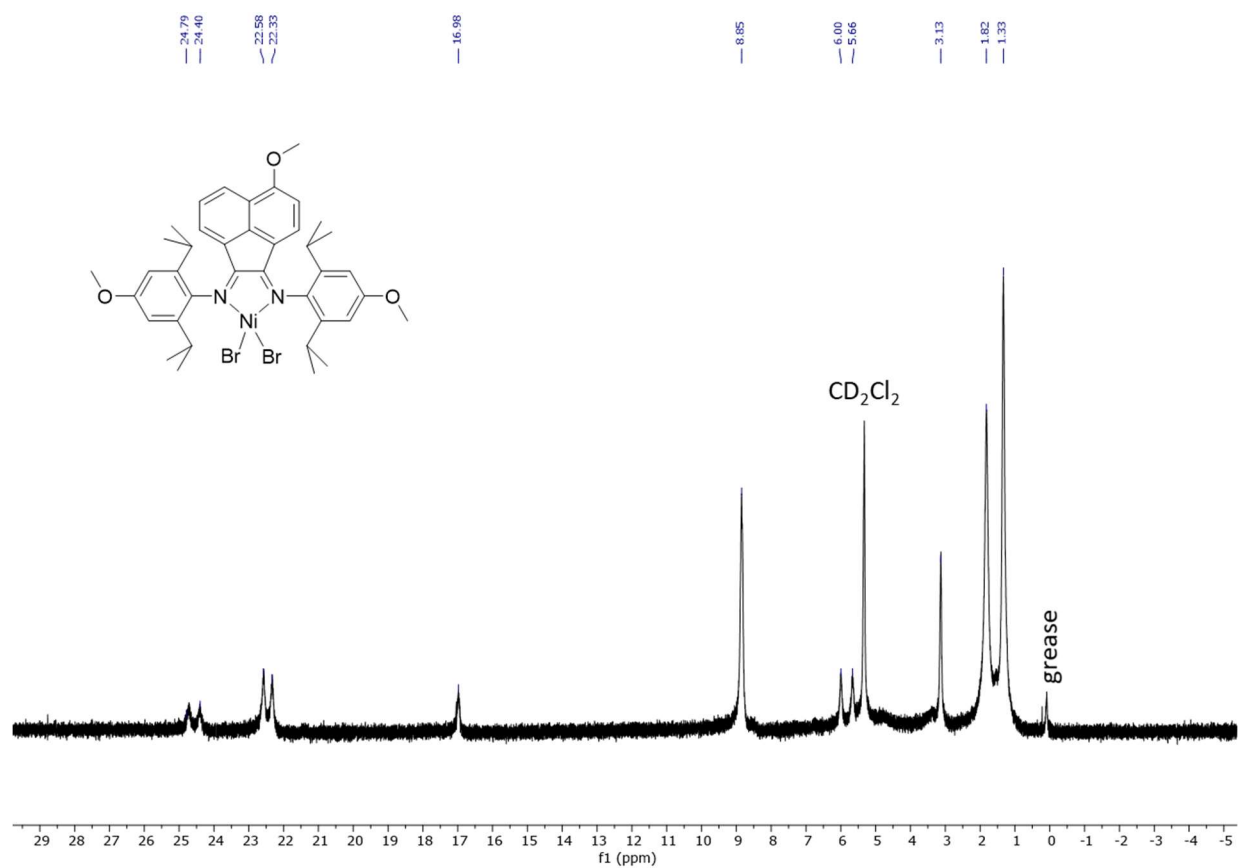


Figure A.106 ¹H NMR (300 MHz, 25 °C, CD₂Cl₂) of **19**, δ, ppm: 1.33, 1.82, 3.13, 5.66, 6.00, 8.85, 16.98, 22.33, 22.58, 24.40, 24.79.

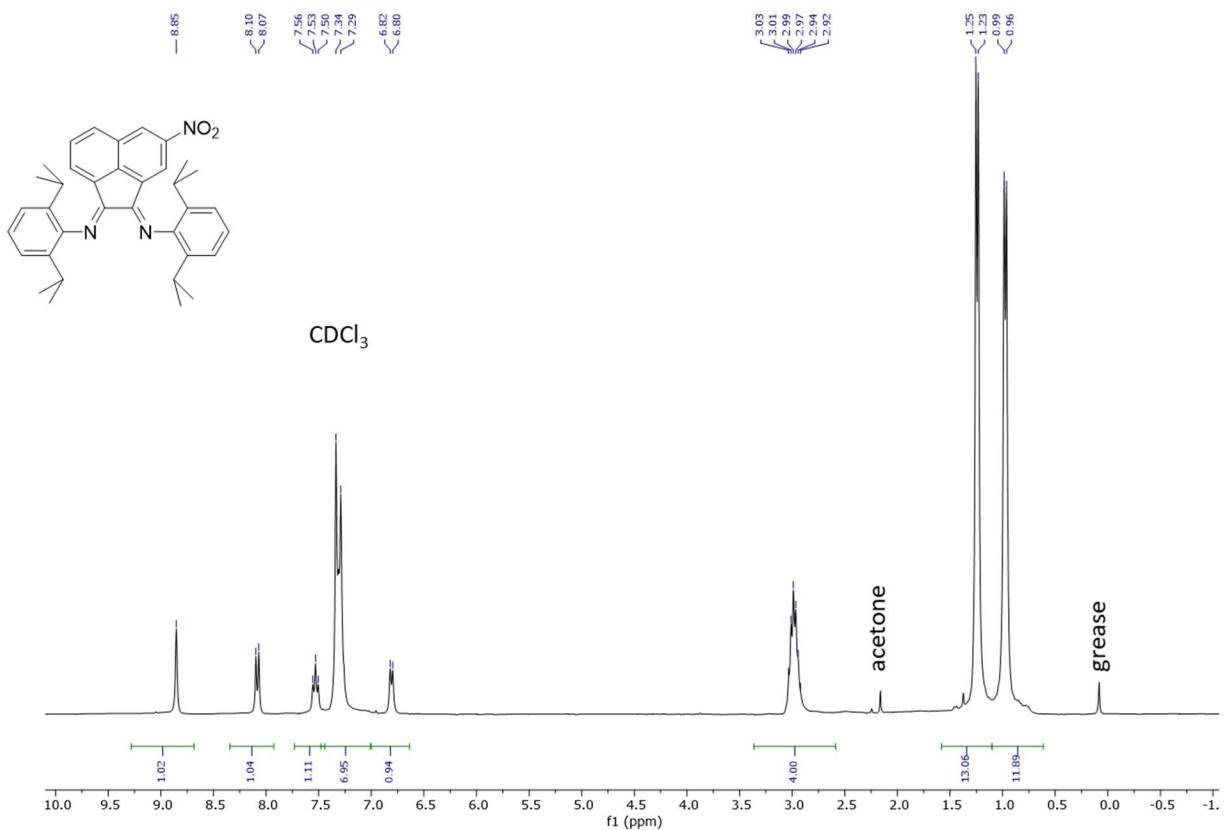


Figure A.107 ^1H NMR (300 MHz, 25°C , CDCl_3) of **L20**, δ , ppm: 0.97 (d, 12H, CH_3), 1.24 (d, 12H, CH_3), 2.98 (m, 4H, CH), 6.81 (d, 1H, aromatic), 7.29-7.34 (m, 7H, aromatic), 7.54 (t, 1H, aromatic), 8.09 (d, 1H, aromatic), 8.85 (s, 1H, aromatic).

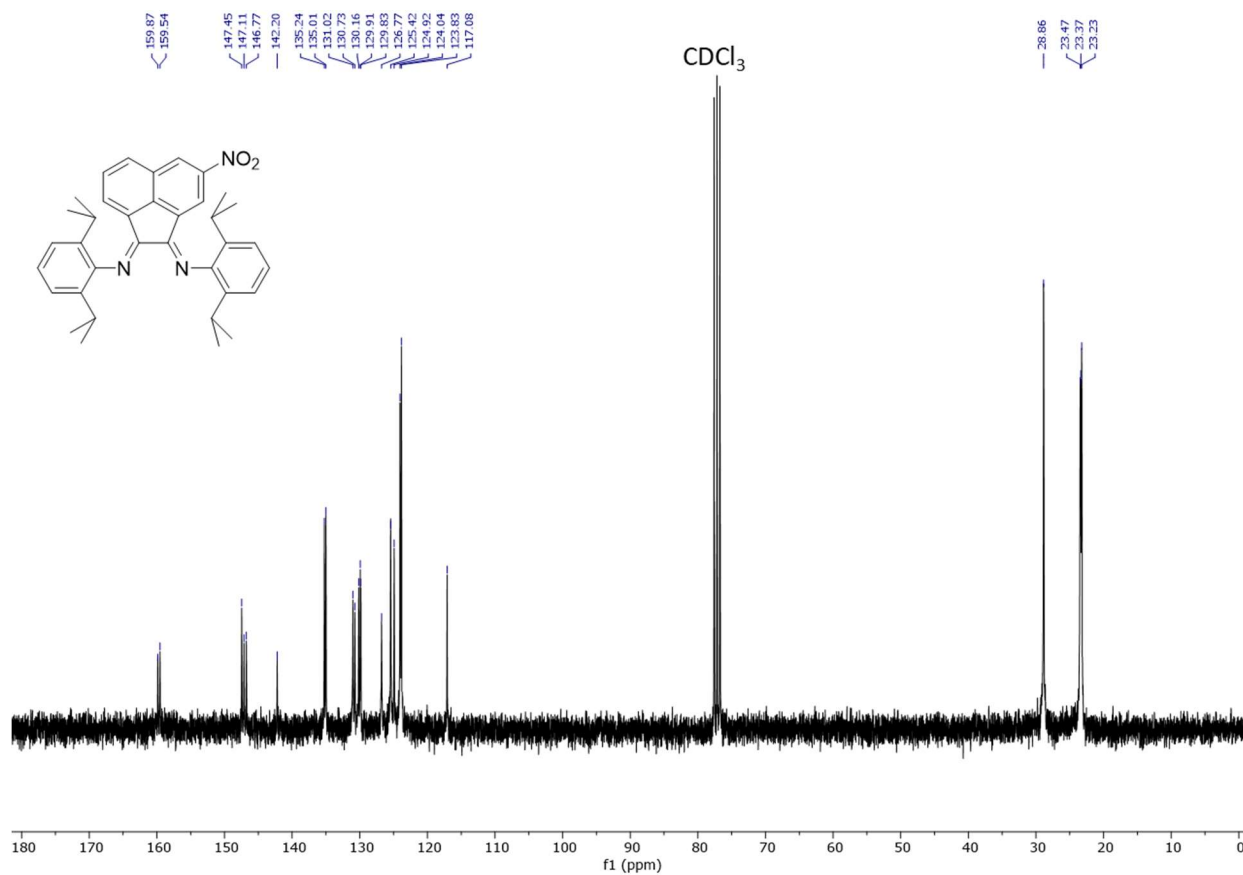


Figure A.108 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of **L20**, δ , ppm: 23.23 (CH_3), 23.37 (CH_3), 23.47 (CH_3), 28.86 (CH), 117.08 (aromatic), 123.83 (aromatic), 124.04 (aromatic), 124.92 (aromatic), 125.42 (aromatic), 126.77 (aromatic), 129.83 (aromatic), 129.91 (aromatic), 130.16 (aromatic), 130.73 (aromatic), 131.02 (aromatic), 135.01 (aromatic), 135.24 (aromatic), 142.20 (aromatic), 146.77 (aromatic), 147.11 (aromatic), 147.45 (aromatic), 159.54 ($\text{C}=\text{N}$), 159.87 ($\text{C}=\text{N}$).

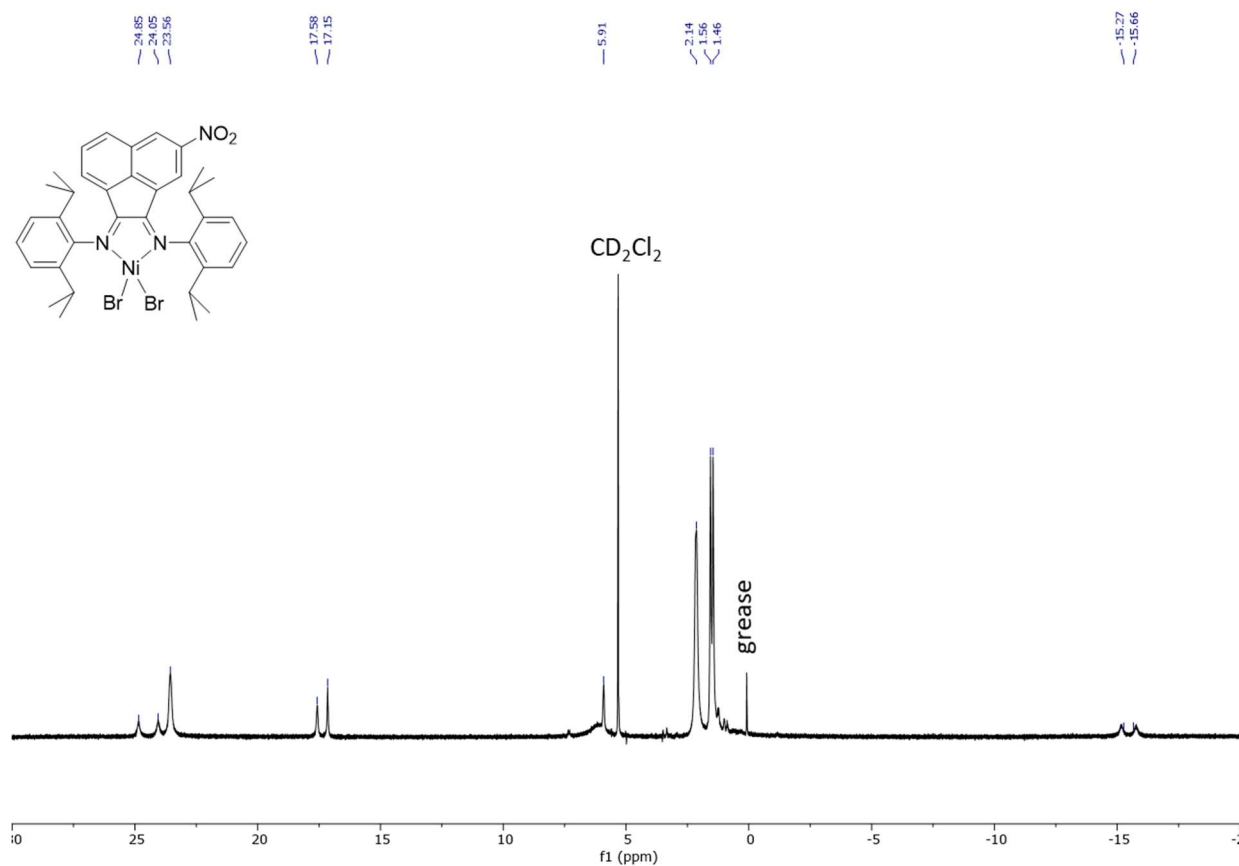


Figure A.109 ^1H NMR (300 MHz, 25 °C, CD_2Cl_2) of **20**, δ , ppm: -15.66, -15.27, 1.46, 1.56, 2.14, 5.91, 17.15, 17.58, 23.56, 24.05, 24.85.

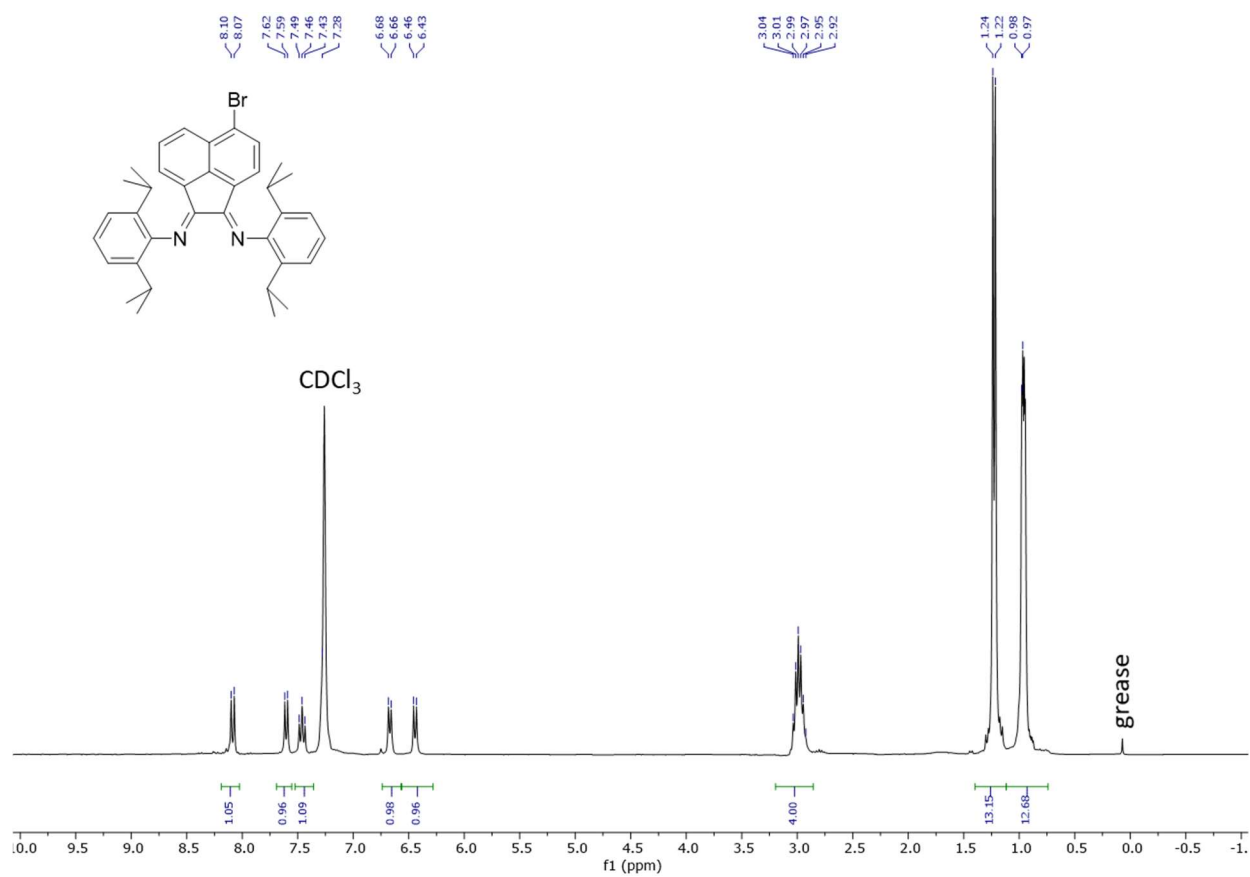


Figure A.110 ^1H NMR (300 MHz, 25 °C, CDCl_3) of **L21**, δ , ppm: 0.97 (d, 12H, CH_3), 1.23 (d, 12H, CH_3), 2.99 (m, 4H, CH), 6.44 (d, 1H, aromatic) 6.67 (d, 1H, aromatic), 7.28 (s, 6H, aromatic), 7.46 (t, 1H, aromatic), 7.61 (d, 1H, aromatic), 8.09 (d, 1H, aromatic).

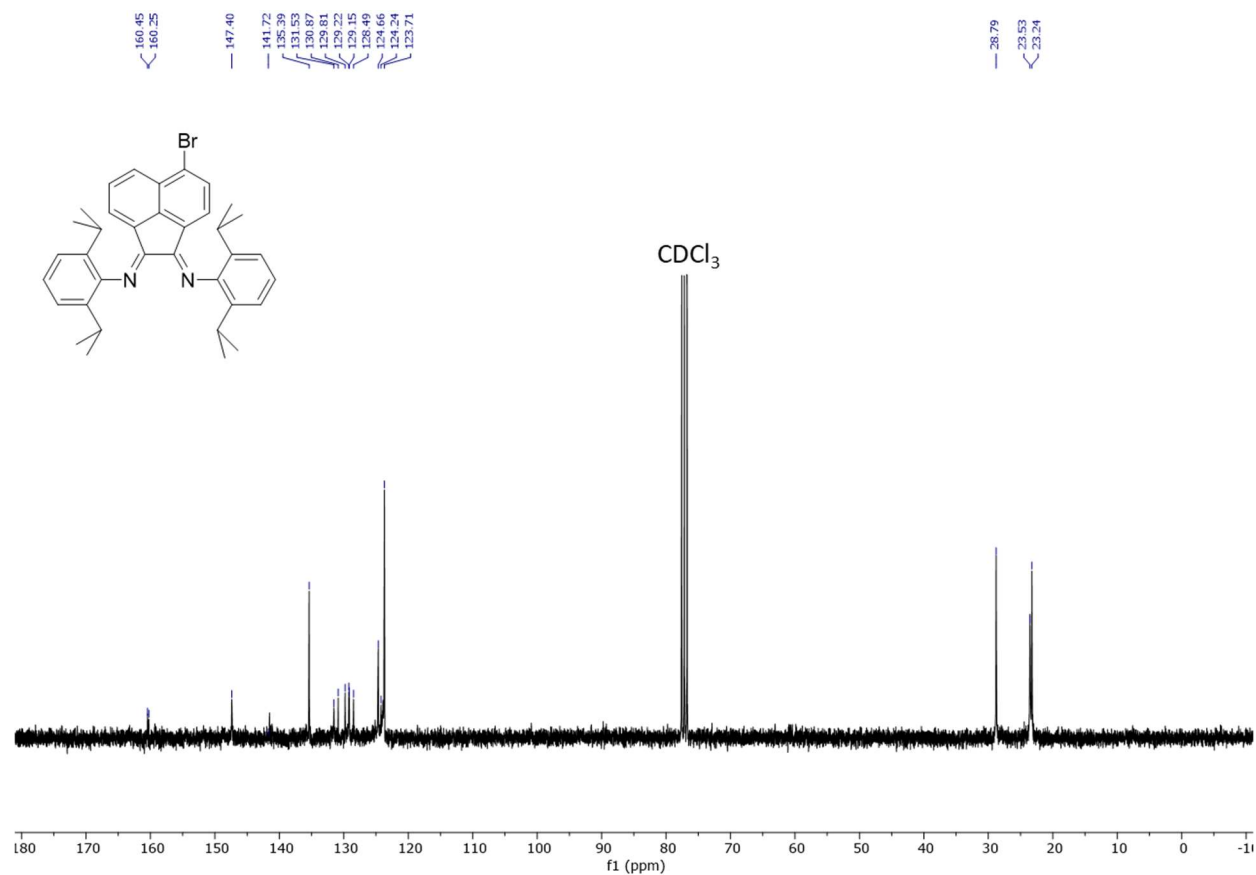


Figure A.111 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of **L21**, δ , ppm: 23.24 (CH_3), 23.53 (CH_3), 28.79 (CH), 123.71 (aromatic), 124.24 (aromatic), 124.66 (aromatic), 128.49 (aromatic), 129.15 (aromatic), 129.22 (aromatic), 129.81 (aromatic), 130.87 (aromatic), 131.53 (aromatic), 135.39 (aromatic), 141.72 (aromatic), 147.40 (aromatic), 160.25 ($\text{C}=\text{N}$), 160.45 ($\text{C}=\text{N}$).

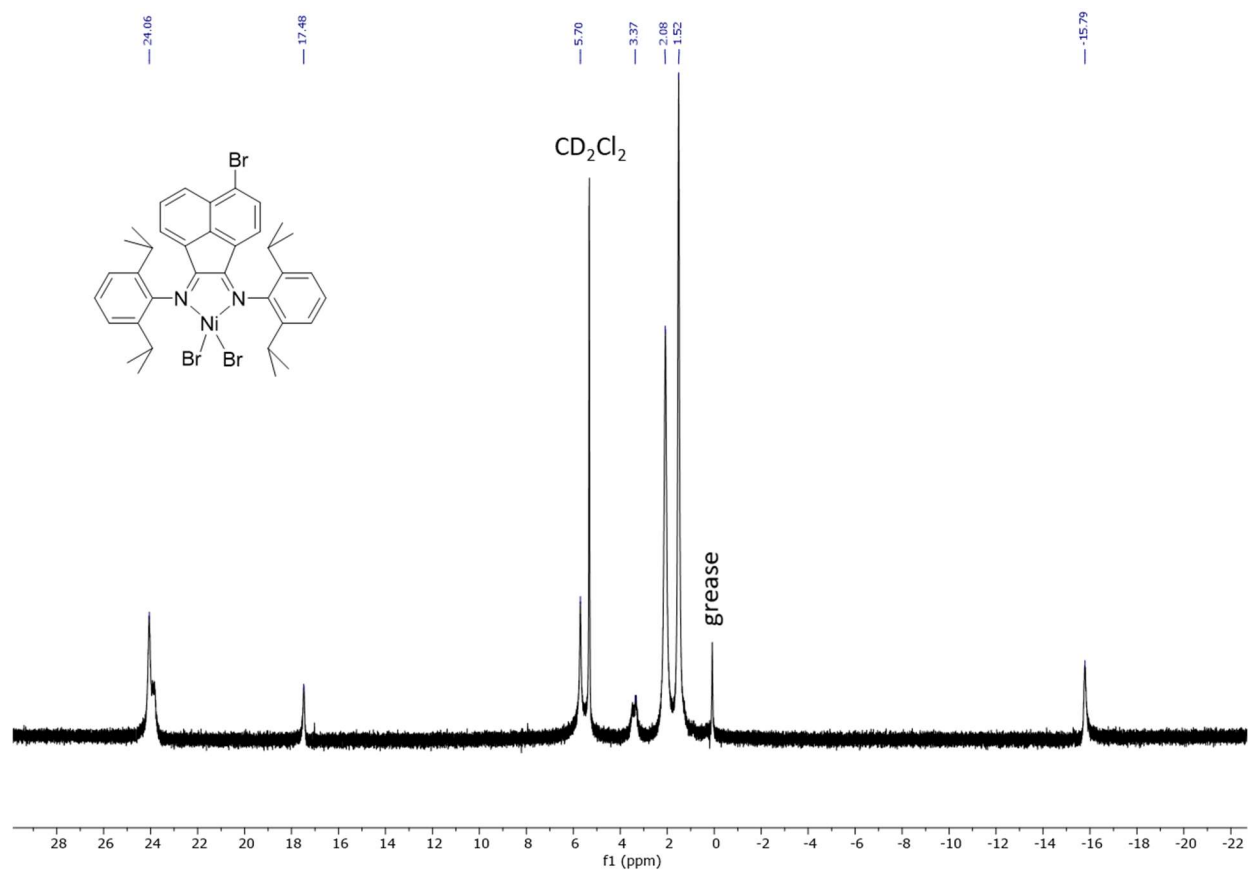


Figure A.112 ^1H NMR (300 MHz, 25°C , CD_2Cl_2) of **21**, δ , ppm: -15.79, 1.52, 2.08, 3.37, 5.7, 17.48, 24.06.

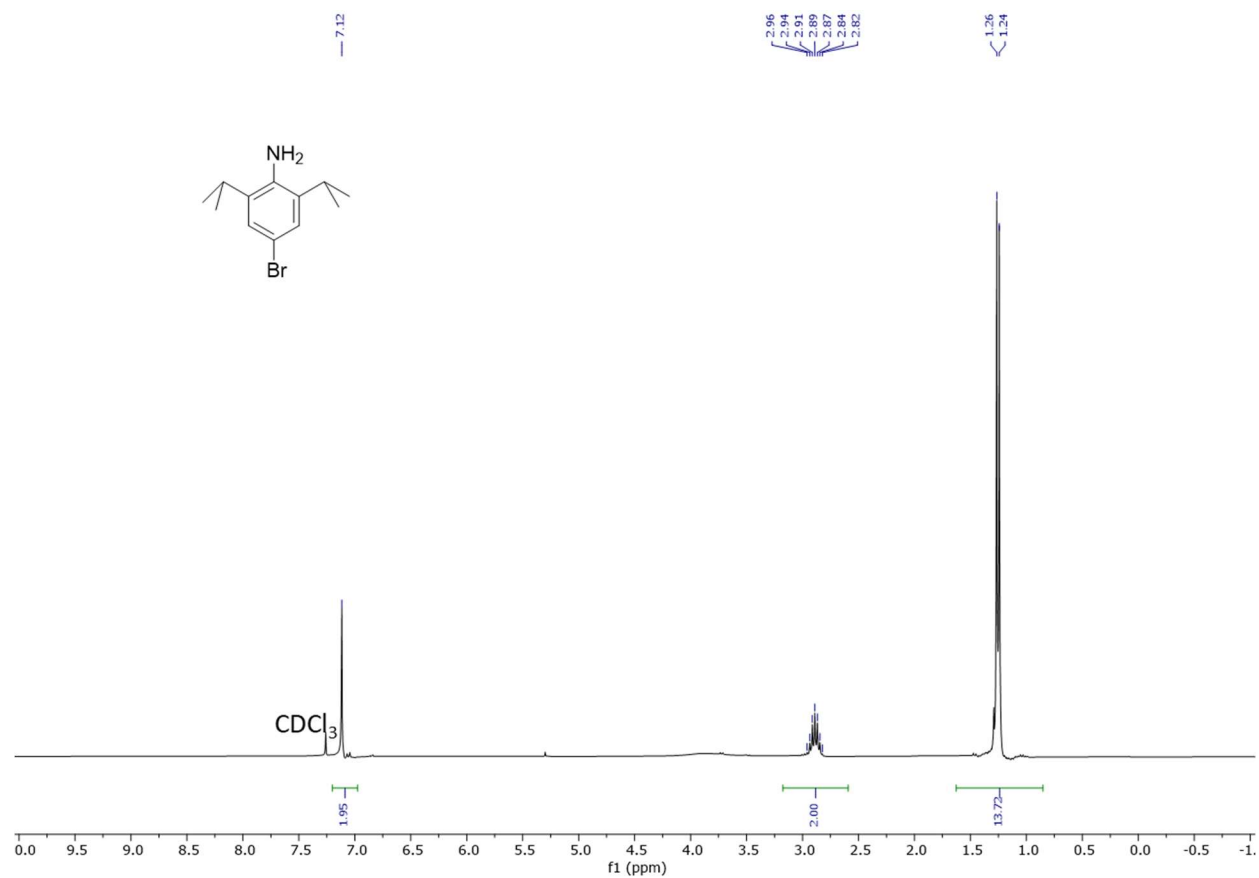


Figure A.113 ¹H NMR (300 MHz, 25 °C, CDCl₃) of 4-bromo-2,6-diisopropylaniline, δ, ppm: 1.25 (d, 12H, CH₃), 2.89 (m, 2H, CH), 7.12 (s, 2H, aromatic).

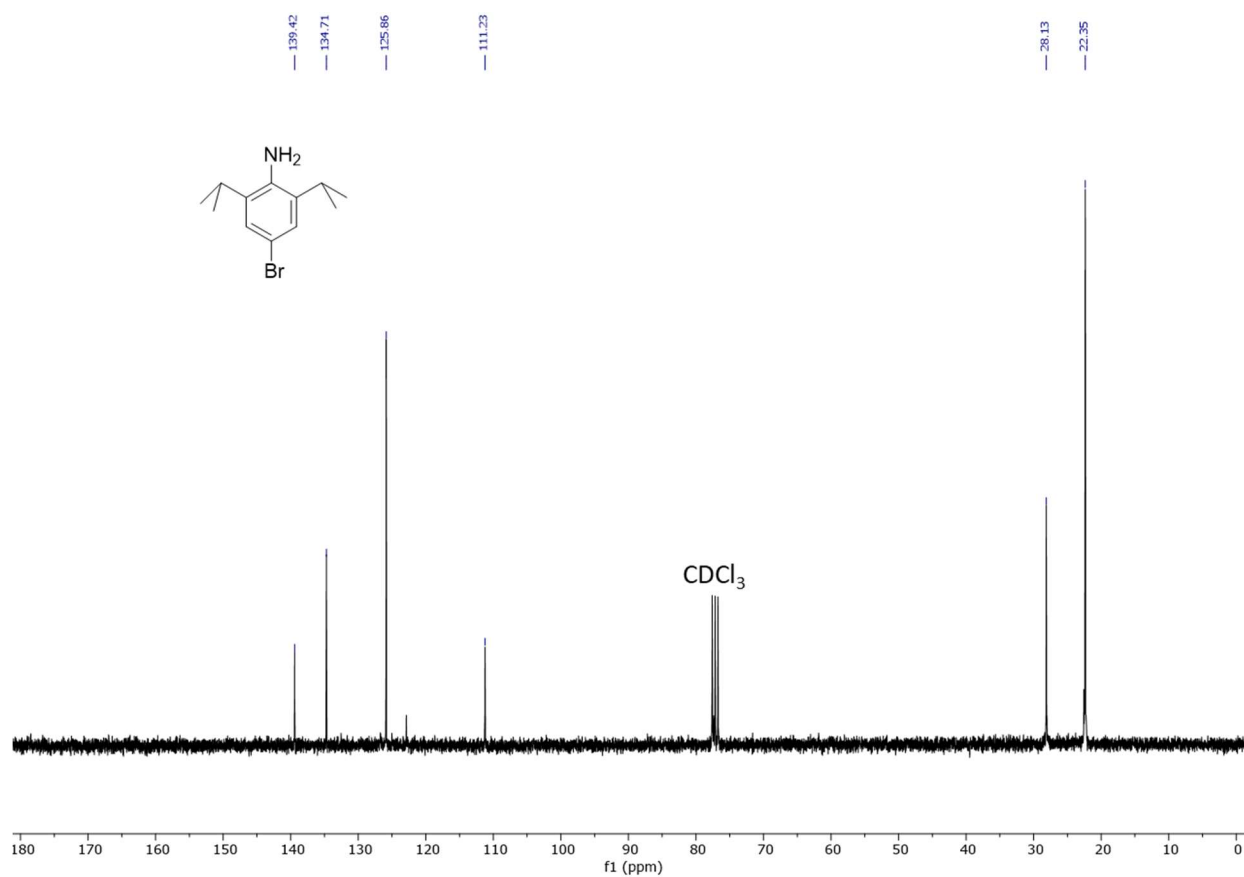


Figure A.114 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of 4-bromo-2,6-diisopropylaniline, δ , ppm: 22.35 (CH_3), 28.13 (CH), 111.23 (aromatic), 125.86 (aromatic), 134.71 (aromatic), 139.42 (aromatic).

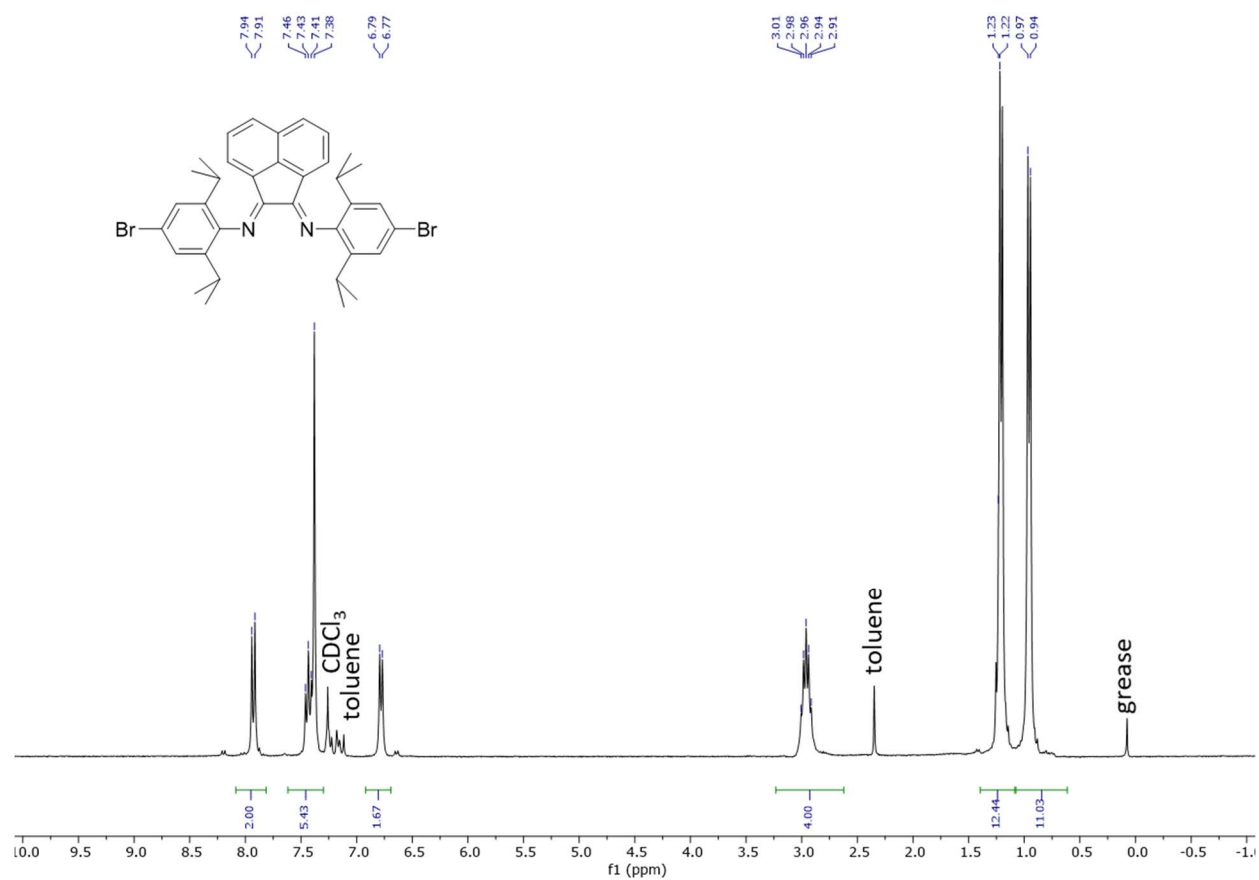


Figure A.115 ¹H NMR (300 MHz, 25 °C, CDCl₃) of **L22**, δ , ppm: 0.95 (d, 12H, CH₃), 1.22 (d, 12H, CH₃), 2.96 (m, 4H, CH), 6.78 (d, 2H, aromatic), 7.38-7.46 (m, 6H, aromatic), 7.93 (d, 2H, aromatic).

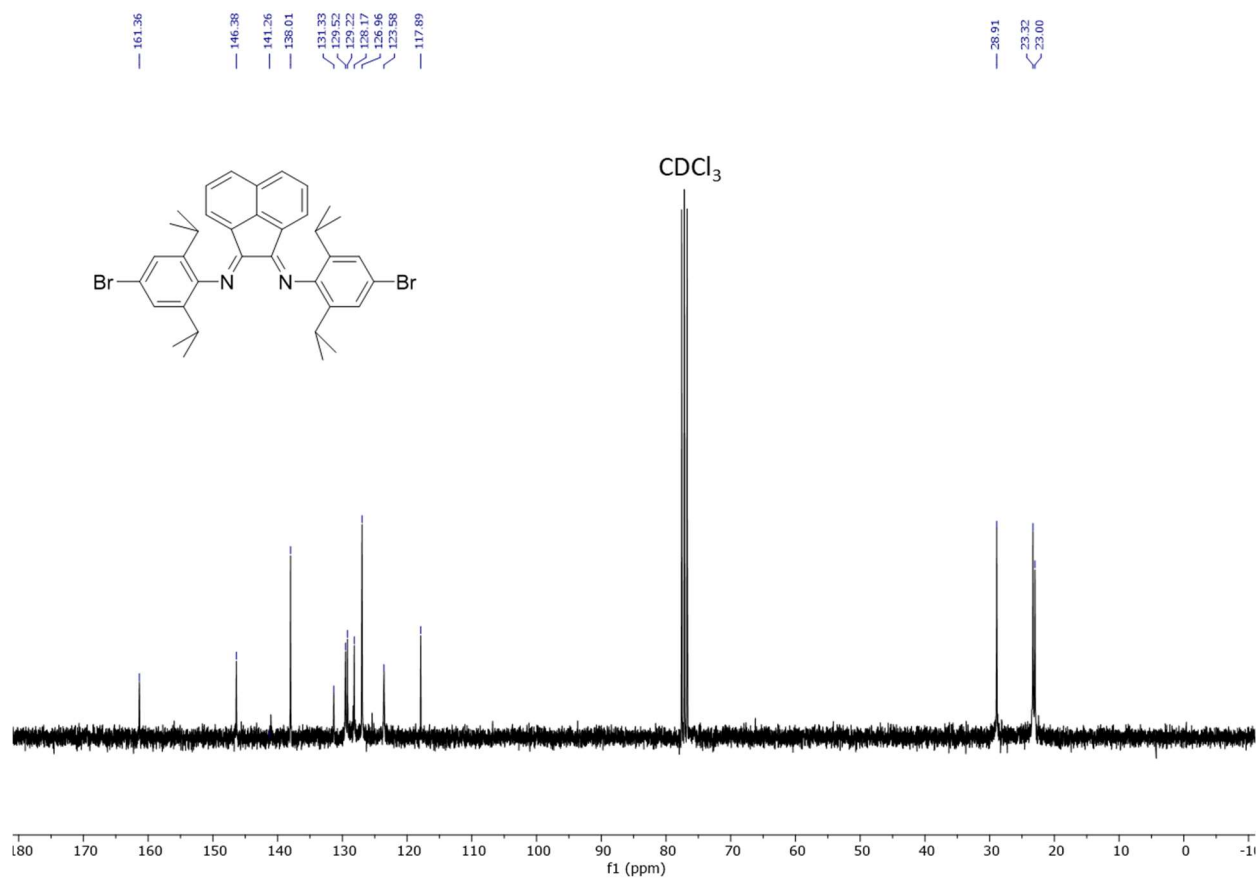


Figure A.116 ^{13}C NMR (300 MHz, 25°C , CDCl_3) of **L22**, δ , ppm: 23.00 (CH_3), 23.32 (CH_3), 28.91 (CH), 117.89 (aromatic), 123.58 (aromatic), 126.96 (aromatic), 128.17 (aromatic), 129.22 (aromatic), 129.52 (aromatic), 131.33 (aromatic), 138.01 (aromatic), 141.26 (aromatic), 146.38 (aromatic), 161.36 ($\text{C}=\text{N}$).

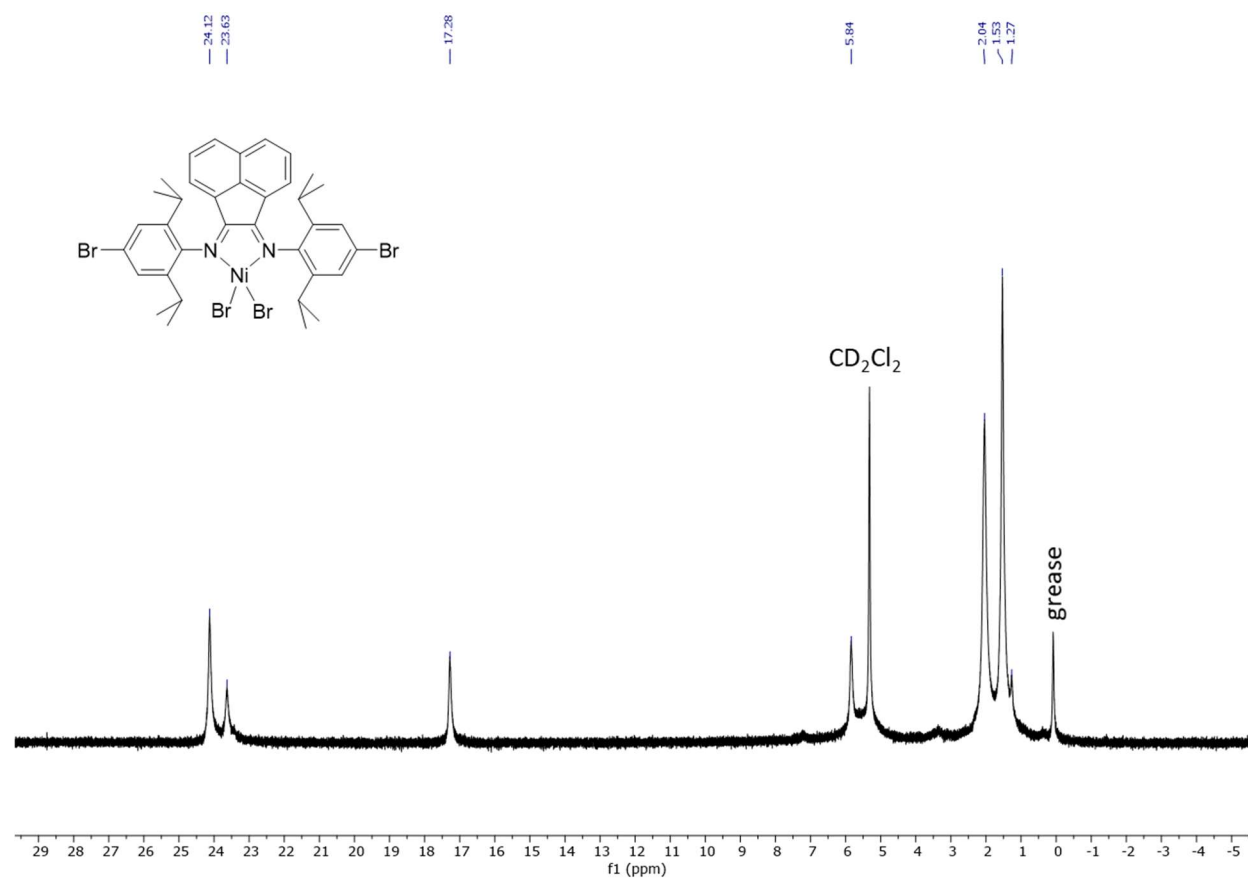


Figure A.117 ^1H NMR (300 MHz, 25 °C, CD_2Cl_2) of **22**, δ , ppm: 1.27, 1.53, 2.04, 5.84, 17.28, 23.63, 24.12.

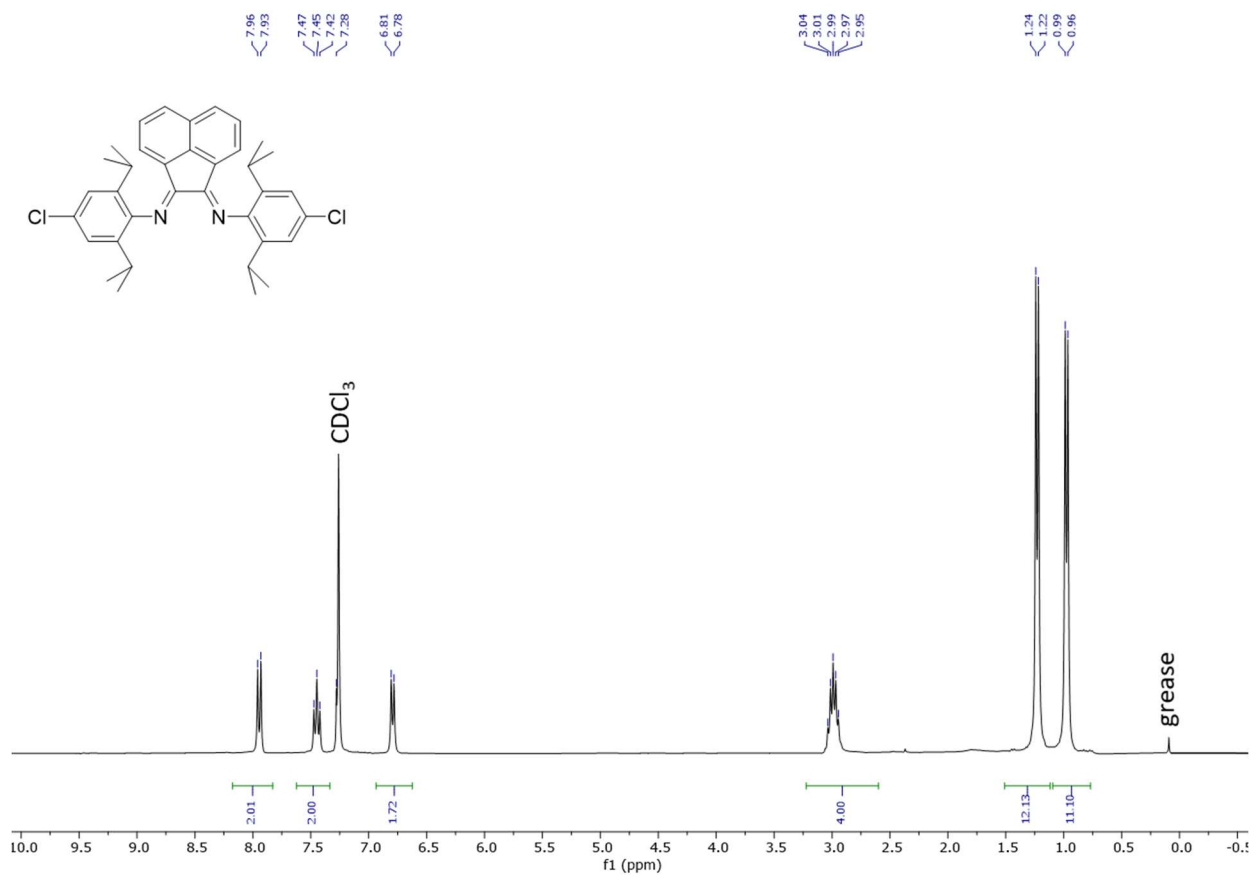


Figure A.118 ¹H NMR (300 MHz, 25 °C, CDCl₃) of **L23**, δ , ppm: 0.97 (d, 12H, CH₃), 1.23 (d, 12H, CH₃), 2.99 (m, 4H, CH), 6.80 (d, 2H, aromatic), 7.28 (s, 4H, aromatic), 7.45 (t, 2H, aromatic), 7.95 (d, 2H, aromatic).

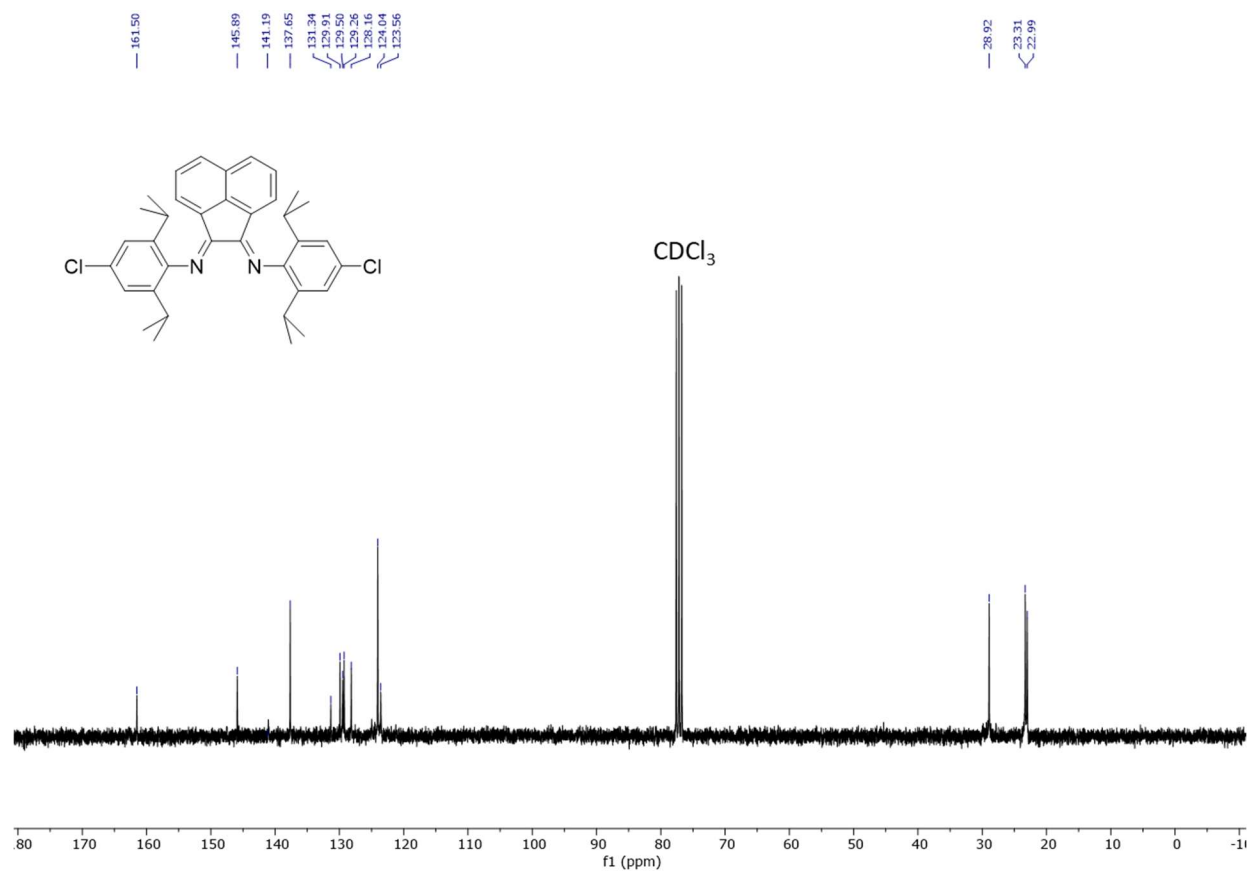


Figure A.119 ^{13}C NMR (300 MHz, 25 °C, CDCl_3) of **L23**, δ , ppm: 22.99 (CH_3), 23.31 (CH_3), 28.92 (CH), 123.56 (aromatic), 124.04 (aromatic), 128.16 (aromatic), 129.26 (aromatic), 129.50 (aromatic), 129.91 (aromatic), 131.34 (aromatic), 137.65 (aromatic), 141.19 (aromatic), 145.89 (aromatic), 161.50 ($\text{C}=\text{N}$).

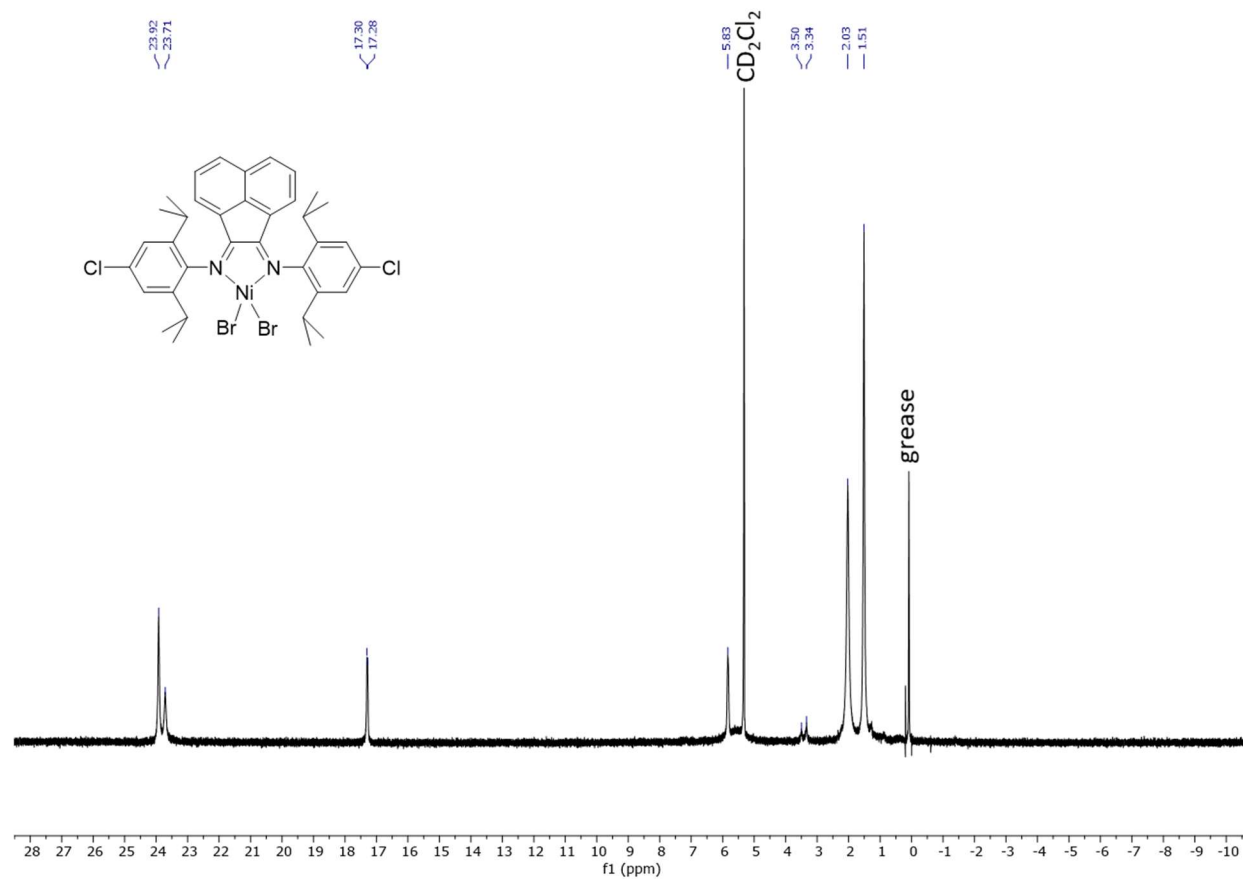


Figure A.120 ^1H NMR (300 MHz, 25 °C, CD_2Cl_2) of **23**, δ , ppm: 1.51, 2.03, 3.34, 3.50, 5.83, 17.28, 17.30, 23.71, 23.92.

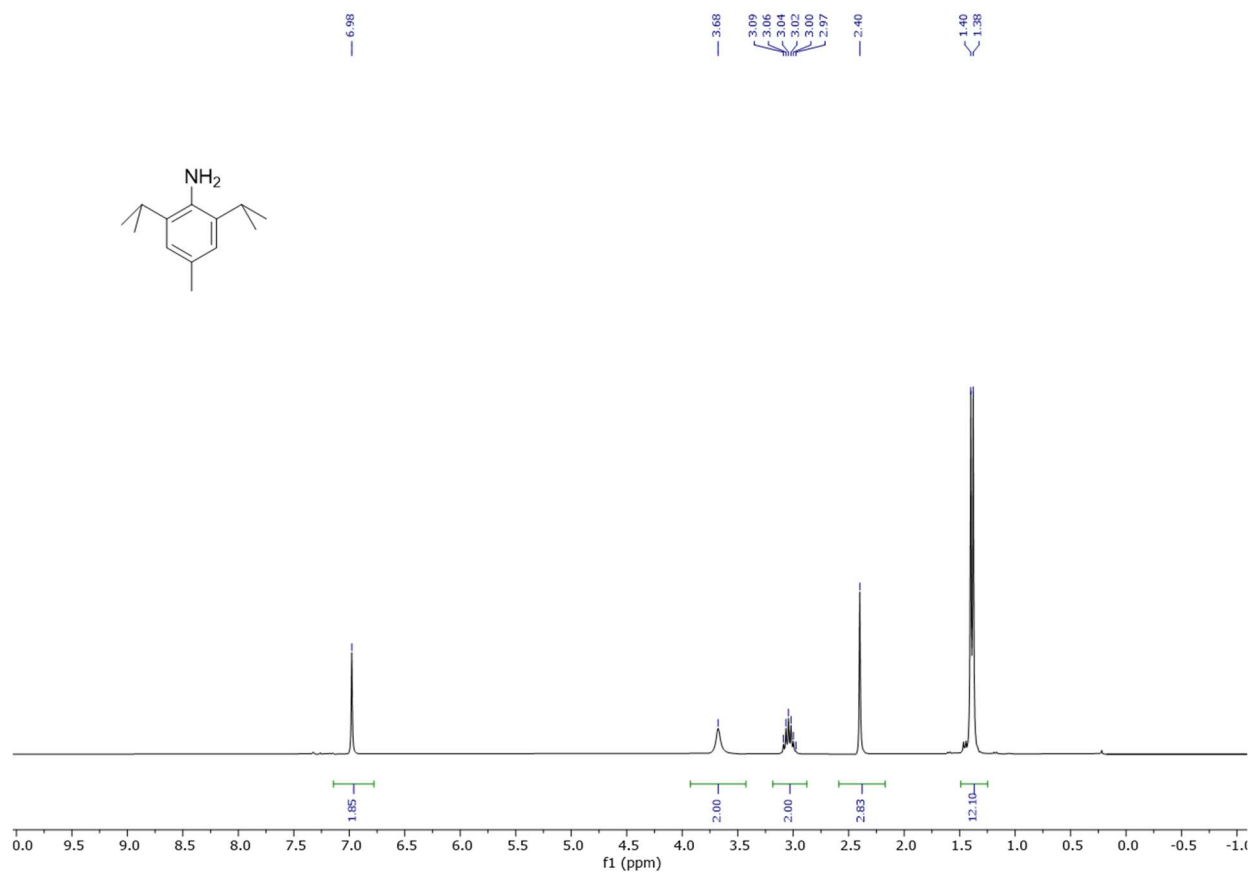


Figure A.121 ¹H NMR (300 MHz, 25 °C, CDCl₃) of 2,6-diisopropyl-4-methylaniline, δ , ppm: 1.39 (d, 12H, CH₃), 2.40 (s, 3H, CH₃), 3.03 (m, 2H, CH), 3.68 (br, 2H, NH₂), 6.98 (s, 2H, aromatic).

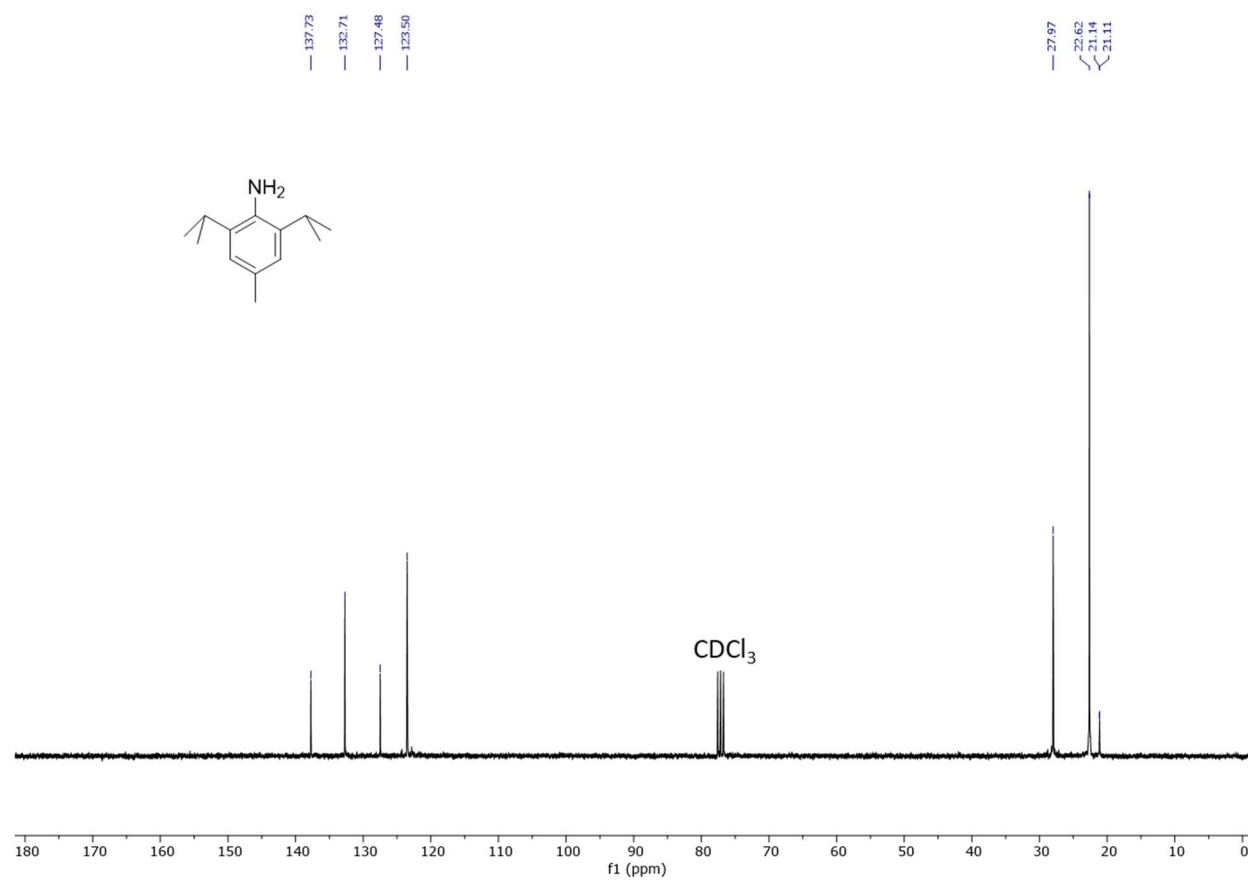


Figure A.122 ¹³C NMR (300 MHz, 25 °C, CDCl₃) of 2,6-diisopropyl-4-methylaniline, δ , ppm: 21.11 (CH₃), 21.14 (CH₃), 22.62 (CH₃), 27.97 (CH), 123.50 (aromatic), 127.48 (aromatic), 132.71 (aromatic), 137.73 (aromatic).

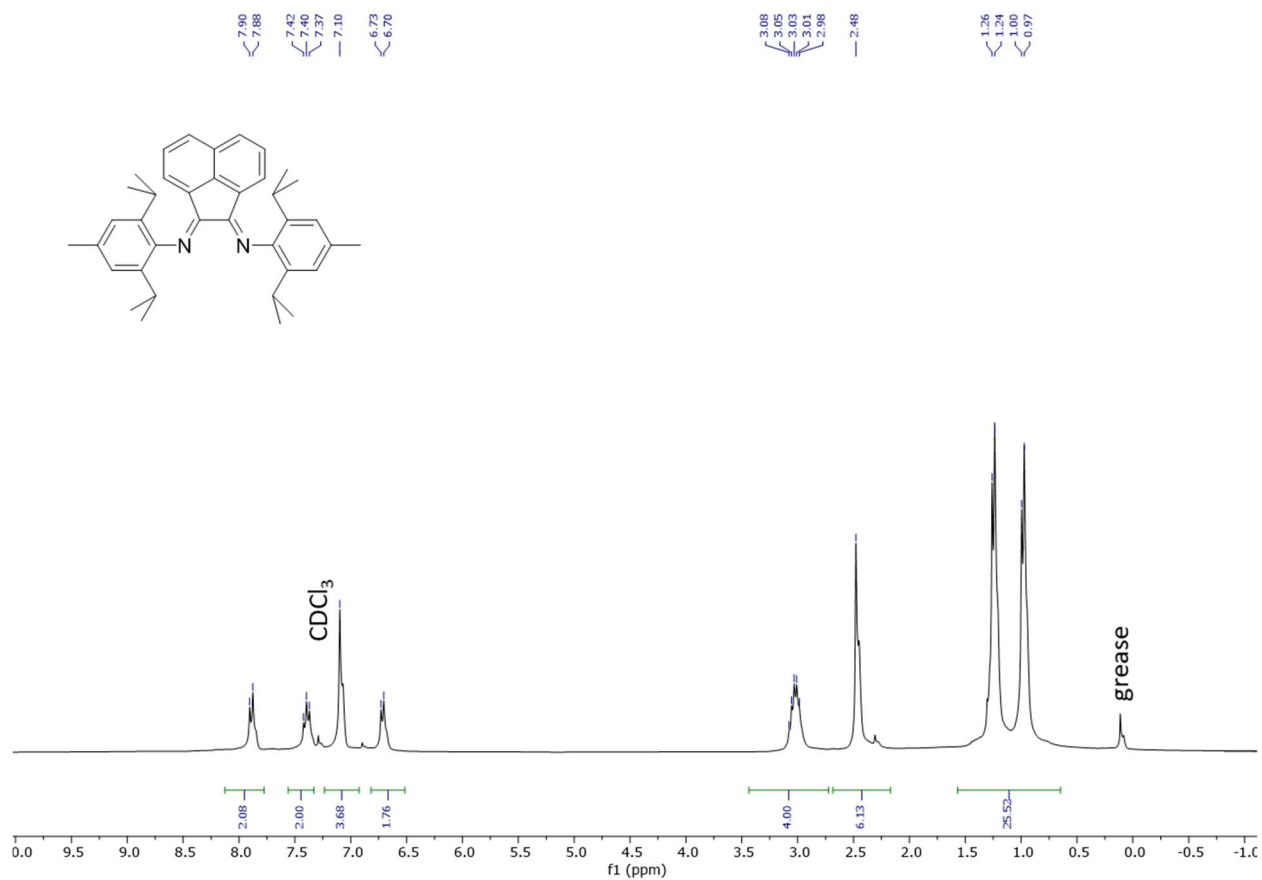


Figure A.123 ^1H NMR (300 MHz, 25°C , CDCl_3) of **L24**, δ , ppm: 0.99 (d, 12H, CH_3), 1.25 (d, 12H, CH_3), 2.48 (s, 6H, CH_3), 3.03 (m, 4H, CH), 6.72 (d, 2H, aromatic), 7.10 (s, 4H, aromatic), 7.40 (t, 2H, aromatic), 7.89 (d, 2H, aromatic).

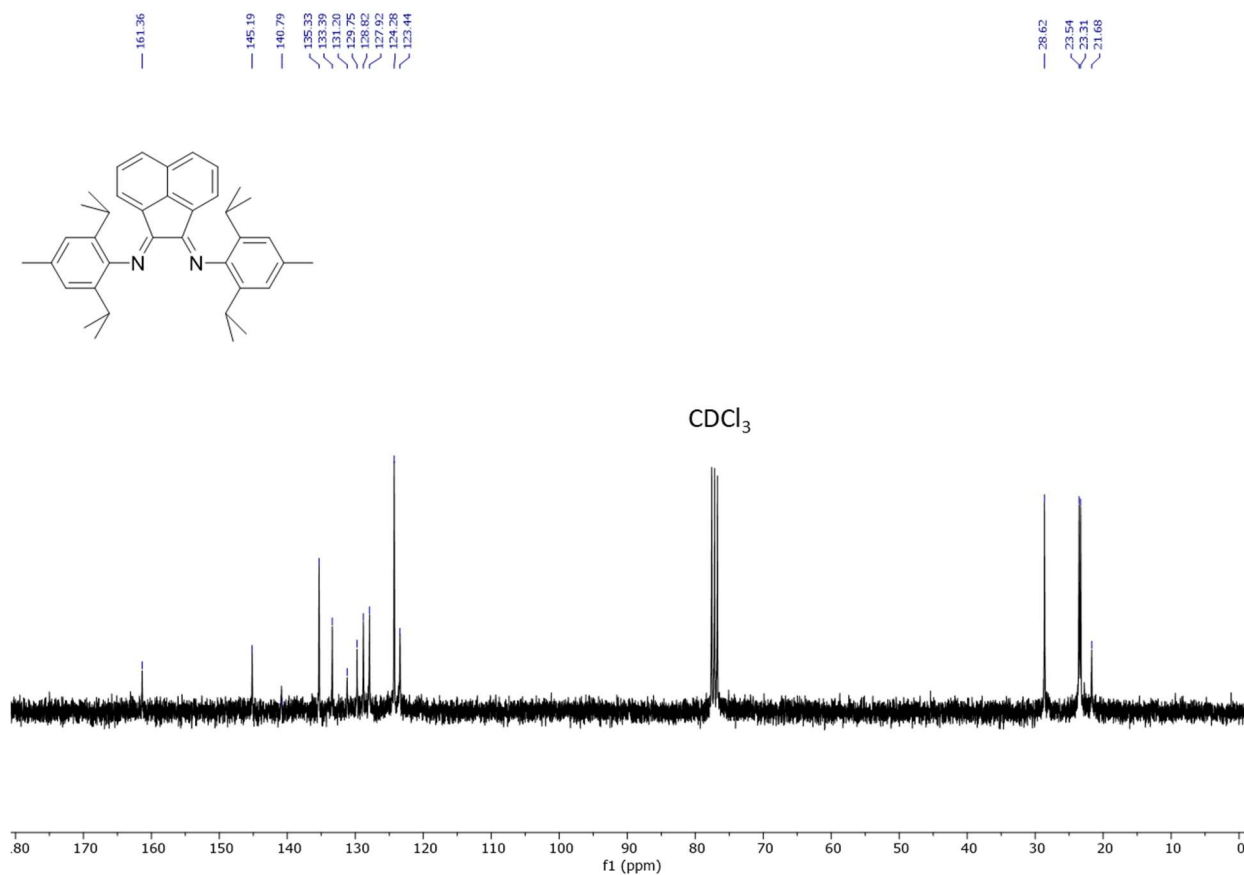


Figure A.124 ^{13}C NMR (300 MHz, 25°C , CDCl_3) of **L24**, δ , ppm: 21.68 (CH_3), 23.31 (CH_3), 23.54 (CH_3), 28.62 (CH), 123.44 (aromatic), 124.28 (aromatic), 127.92 (aromatic), 128.82 (aromatic), 129.75 (aromatic), 131.20 (aromatic), 133.39 (aromatic), 135.33 (aromatic), 140.79 (aromatic), 145.19 (aromatic), 161.36 ($\text{C}=\text{N}$).

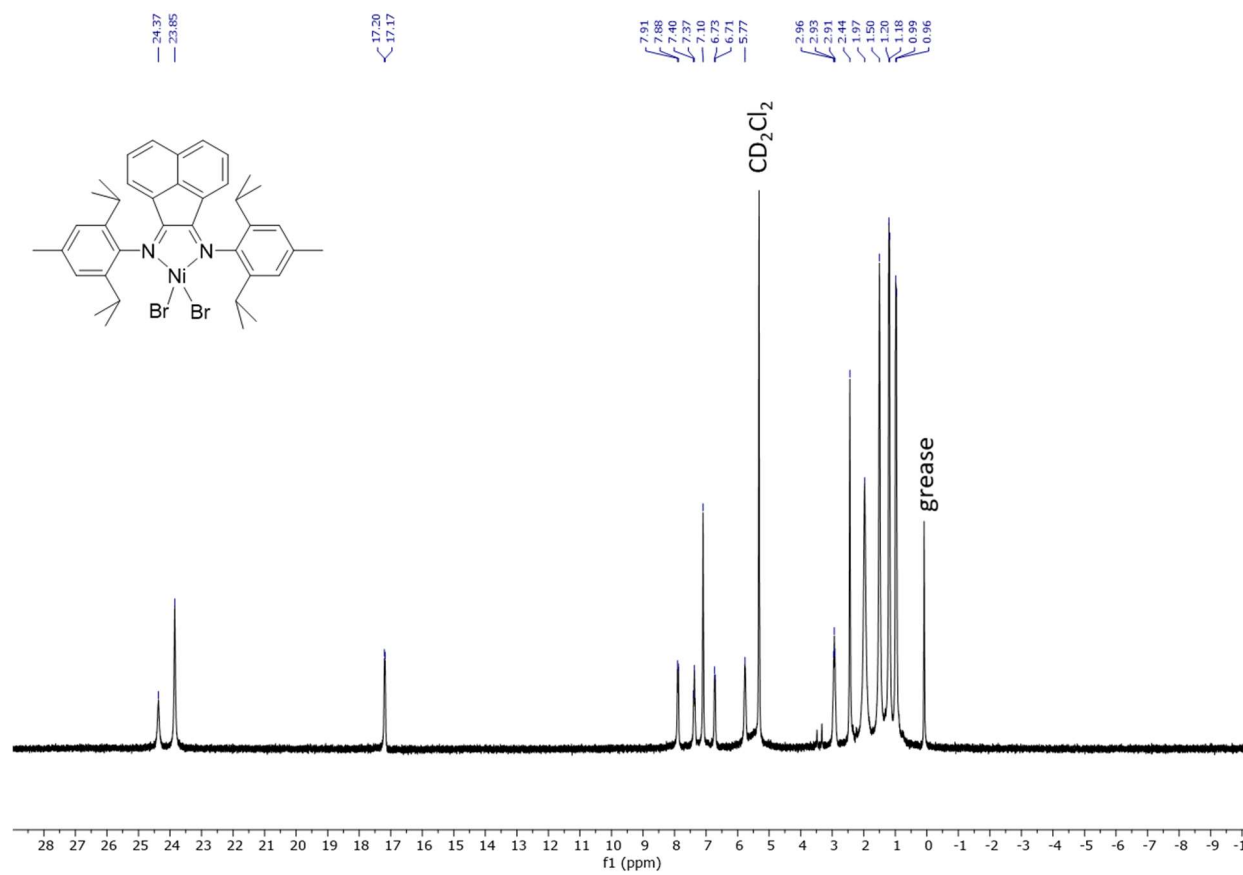


Figure A.125 ¹H NMR (300 MHz, 25 °C, CD₂Cl₂) of **24**, δ, ppm: 0.97, 1.19, 1.50, 1.97, 2.44, 2.93, 5.77, 6.72, 7.10, 7.38, 7.89, 17.19, 23.85, 24.37.

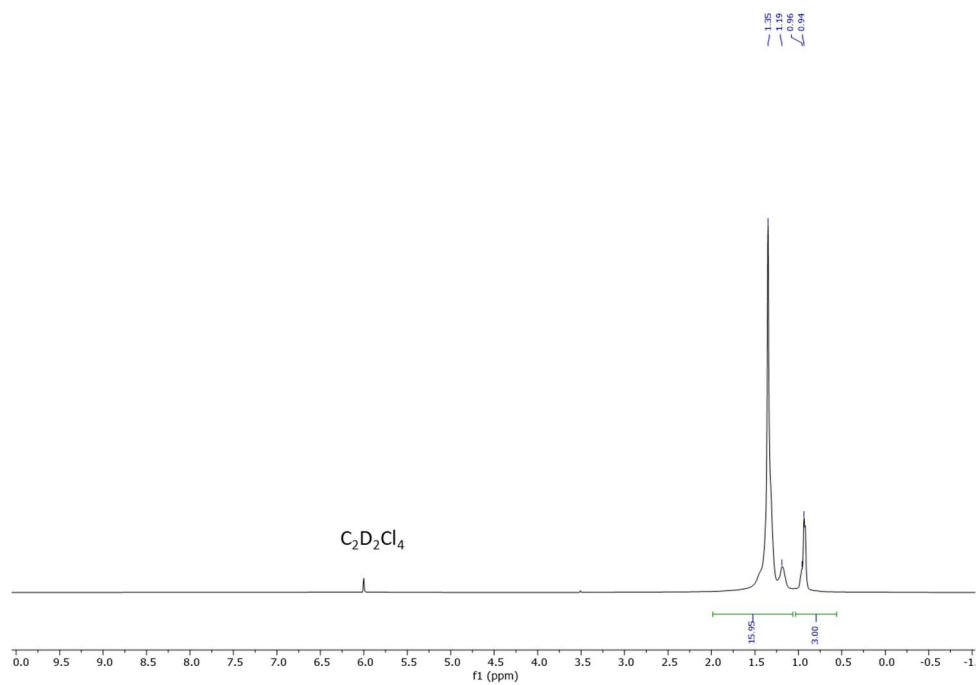


Figure A.126 Representative ^1H NMR (400 MHz, 100 $^\circ\text{C}$, $\text{C}_2\text{D}_2\text{Cl}_4$), δ , ppm of PE obtained using **13** (Table 5.1, entry 1).

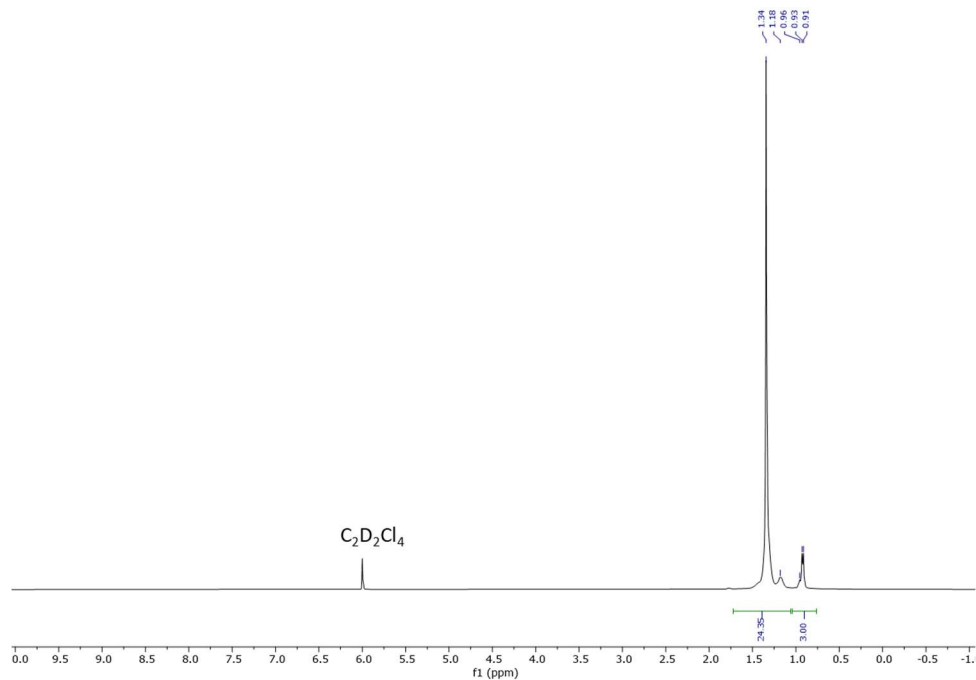


Figure A.127 Representative ^1H NMR (400 MHz, 100 $^\circ\text{C}$, $\text{C}_2\text{D}_2\text{Cl}_4$), δ , ppm of PE obtained using **14** (Table 5.1, entry 2).

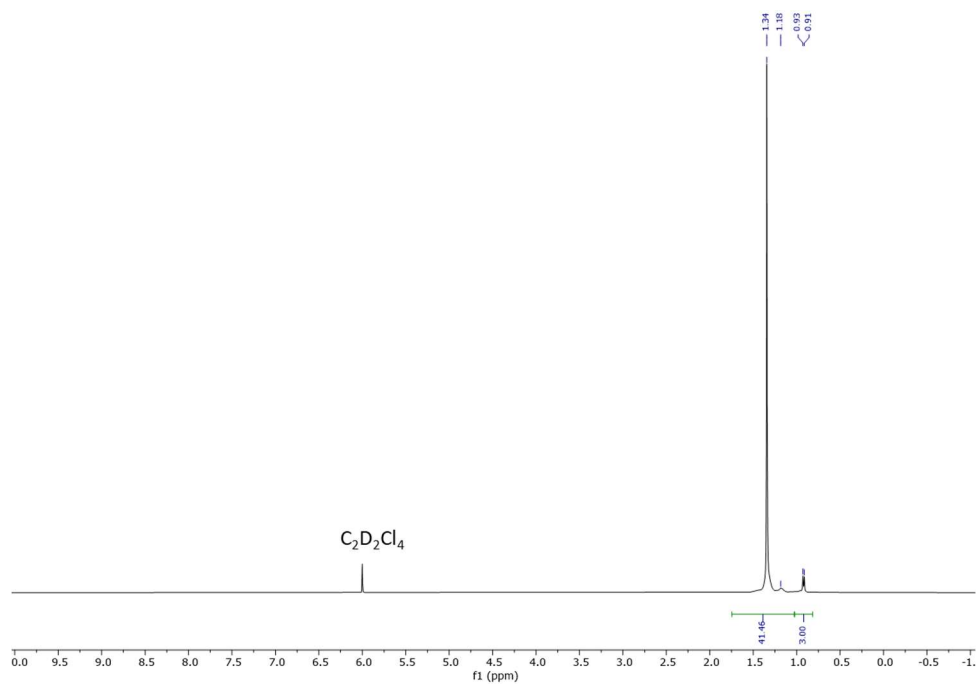


Figure A.128 Representative ^1H NMR (400 MHz, 100°C , $\text{C}_2\text{D}_2\text{Cl}_4$), δ , ppm of PE obtained using **15** (Table 5.1, entry 3).

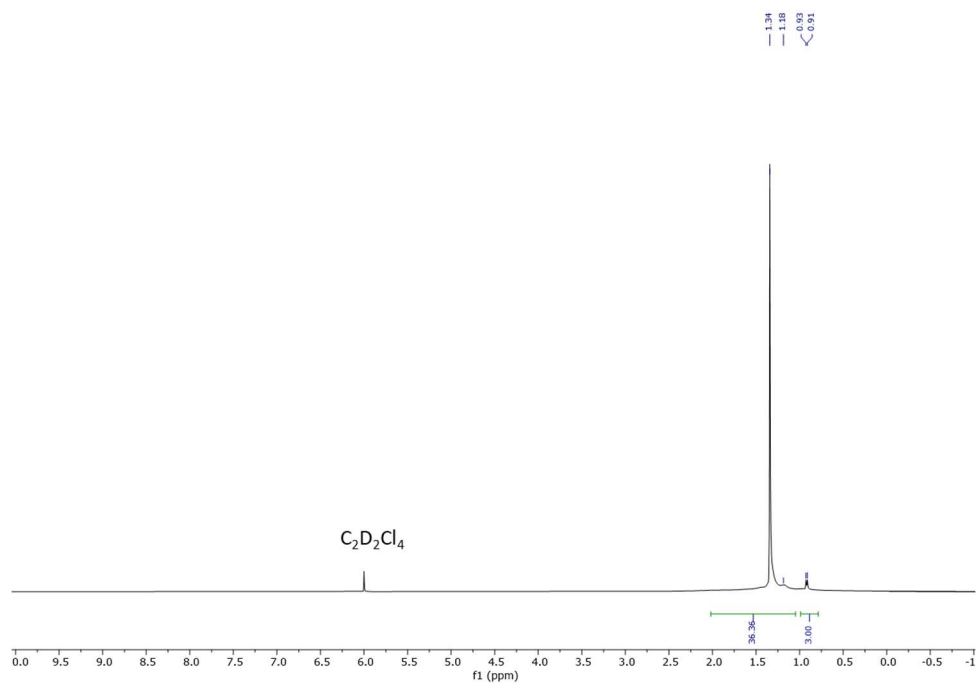


Figure A.129 Representative ^1H NMR (400 MHz, 100°C , $\text{C}_2\text{D}_2\text{Cl}_4$), δ , ppm of PE obtained using **16** (Table 5.1, entry 4).

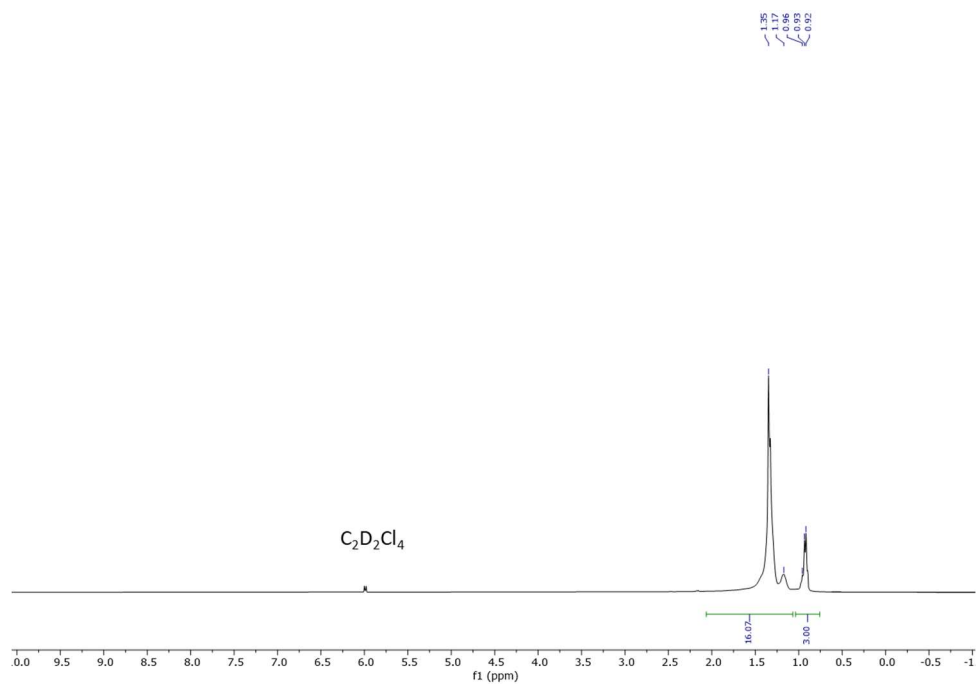


Figure A.130 Representative ¹H NMR (400 MHz, 100 °C, C₂D₂Cl₄), δ, ppm of PE obtained using **17** (Table 5.1, entry 5).

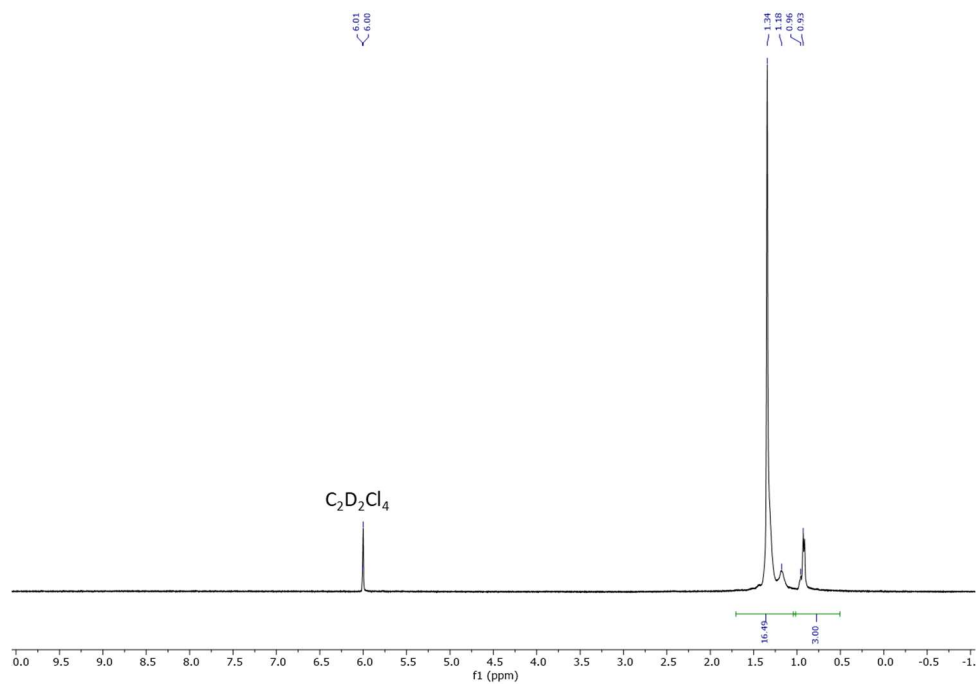


Figure A.131 Representative ¹H NMR (400 MHz, 100 °C, C₂D₂Cl₄), δ, ppm of PE obtained using **18** (Table 5.1, entry 6).

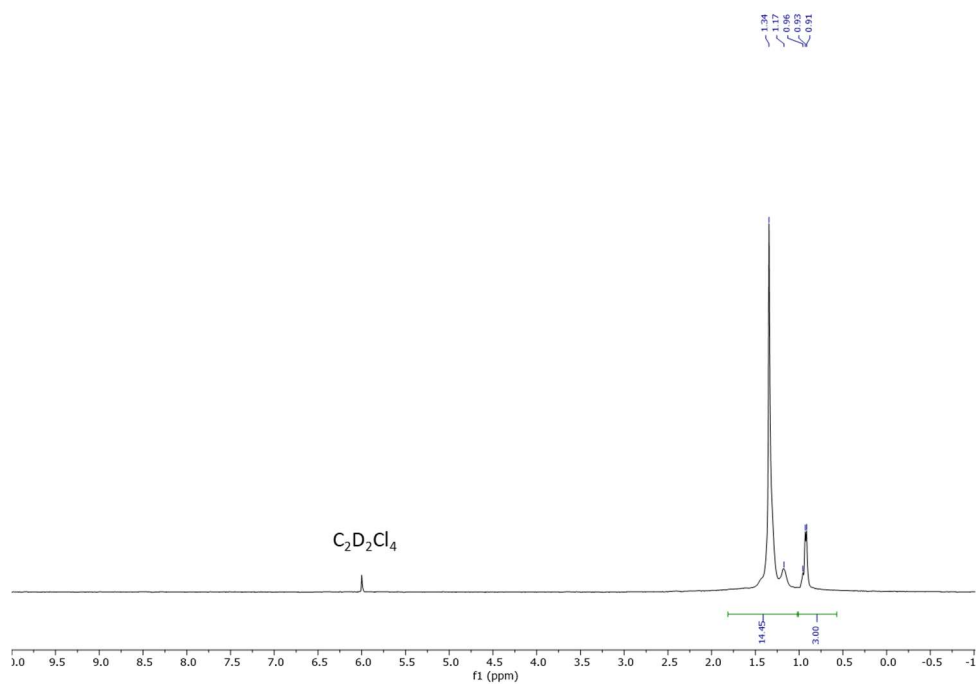


Figure A.132 Representative ¹H NMR (400 MHz, 100 °C, C₂D₂Cl₄), δ, ppm of PE obtained using **19** (Table 5.1, entry 7).

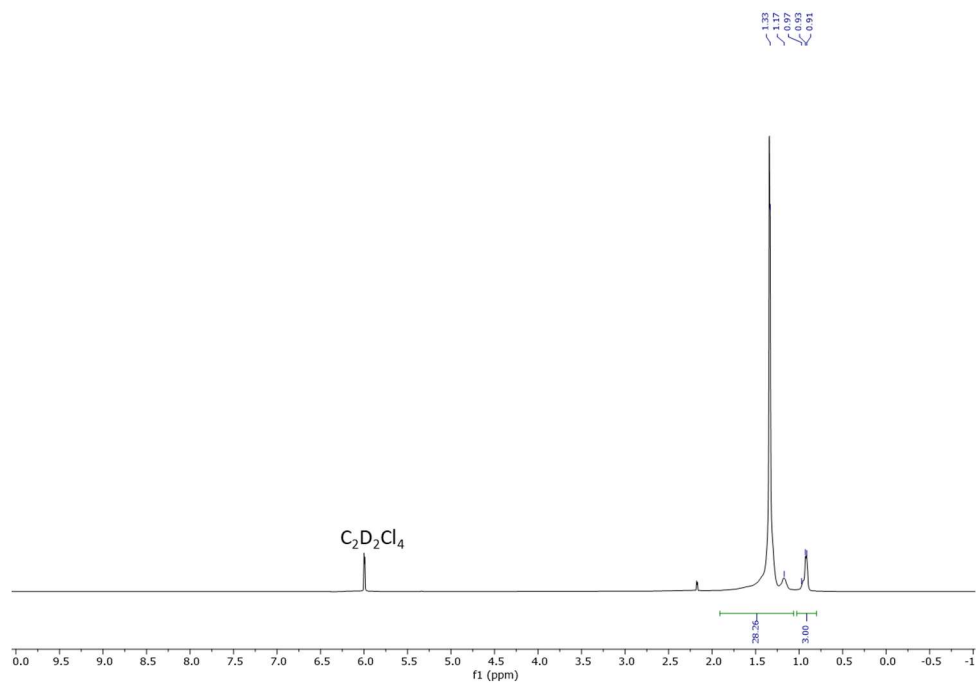


Figure A.133 Representative ¹H NMR (400 MHz, 100 °C, C₂D₂Cl₄), δ, ppm of PE obtained using **20** (Table 5.2, entry 1).

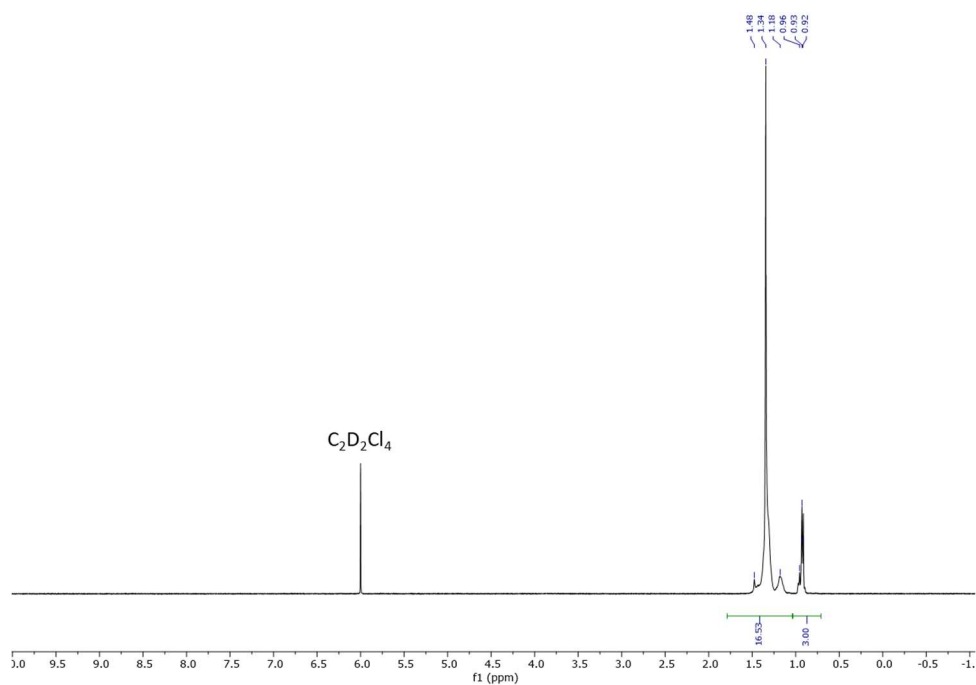


Figure A.134 Representative 1H NMR (400 MHz, 100 °C, $C_2D_2Cl_4$), δ , ppm of PE obtained using **21** (Table 5.2, entry 2).

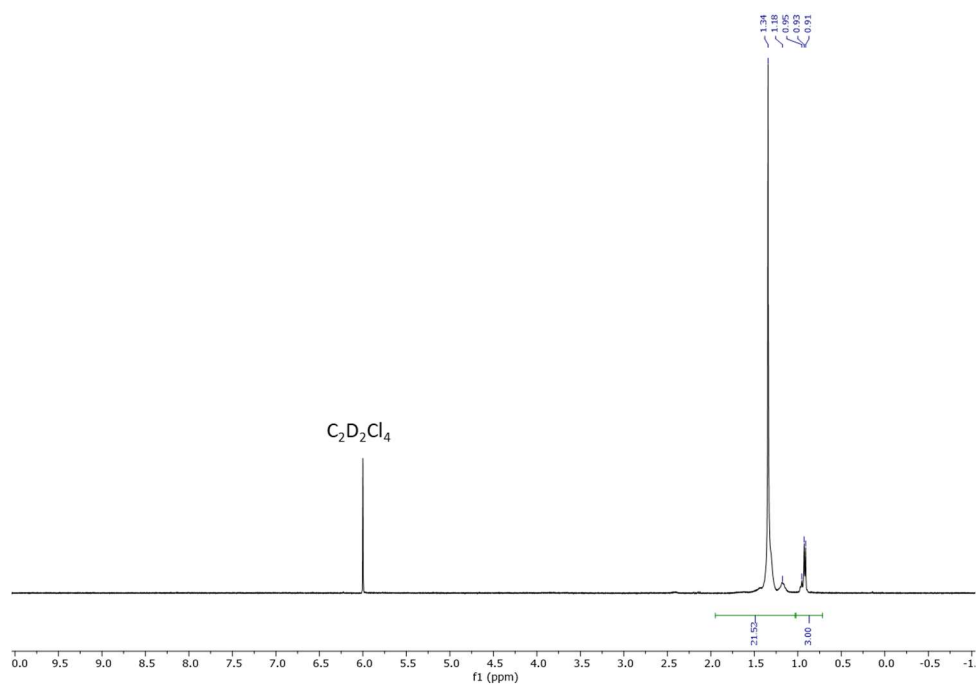


Figure A.135 Representative 1H NMR (400 MHz, 100 °C, $C_2D_2Cl_4$), δ , ppm of PE obtained using **22** (Table 5.2, entry 3).

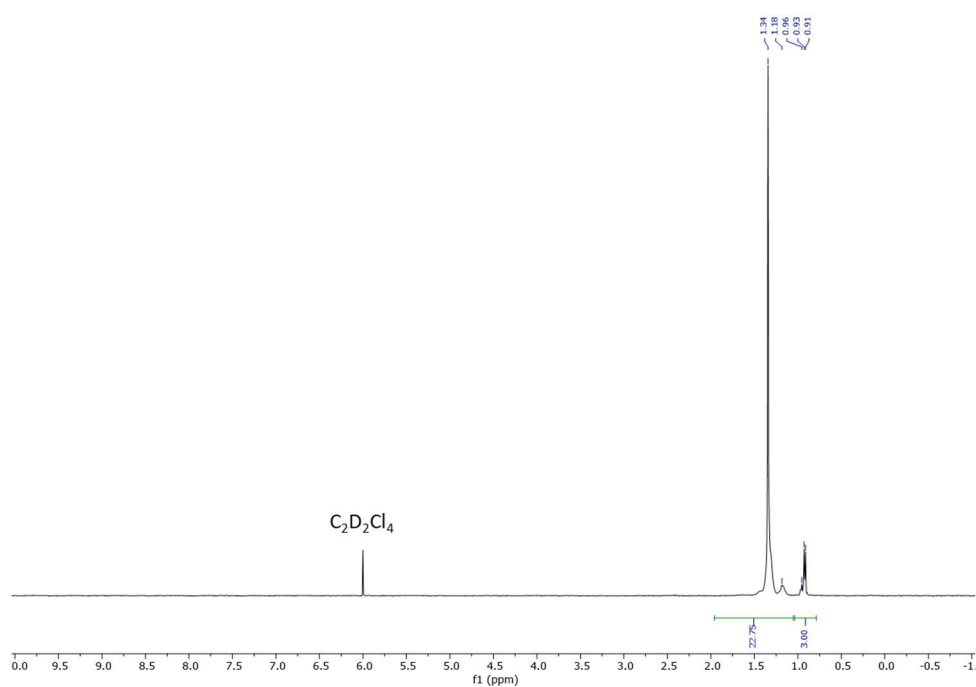


Figure A.136 Representative ^1H NMR (400 MHz, 100 $^\circ\text{C}$, $\text{C}_2\text{D}_2\text{Cl}_4$), δ , ppm of PE obtained using **23** (Table 5.2, entry 4).

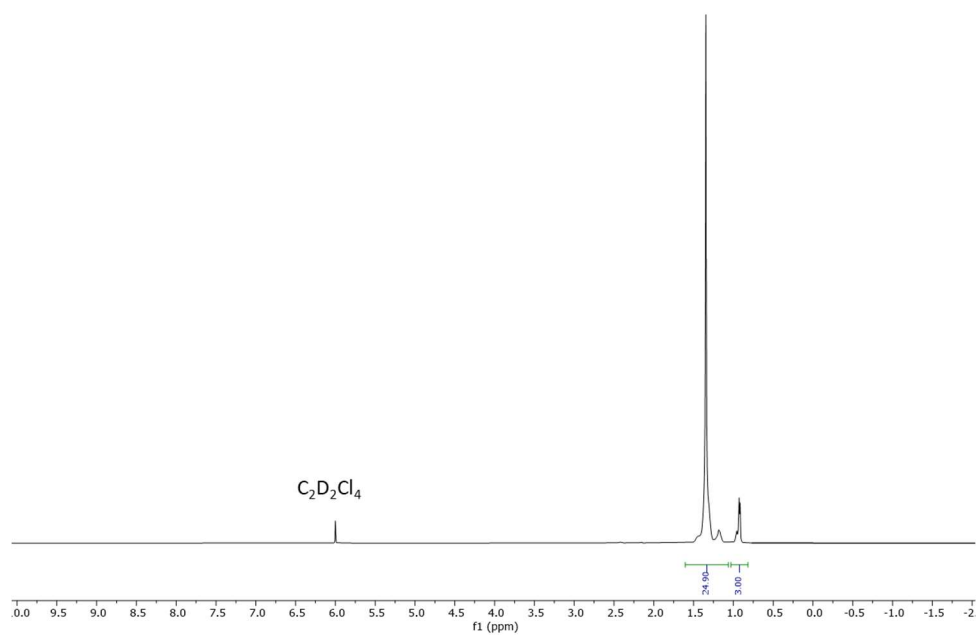


Figure A.137 Representative ^1H NMR (400 MHz, 100 $^\circ\text{C}$, $\text{C}_2\text{D}_2\text{Cl}_4$), δ , ppm of PE obtained using **24** (Table 5.2, entry 5).

A.6.2 Cyclic Voltammetry

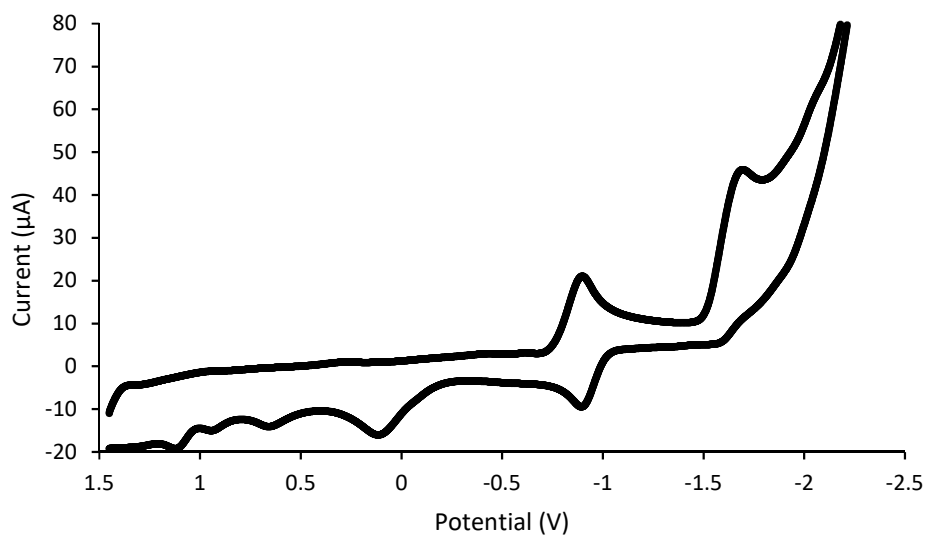


Figure A.138 Cyclic voltammogram of catalyst **13** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.895 V) versus Fc/Fc⁺.

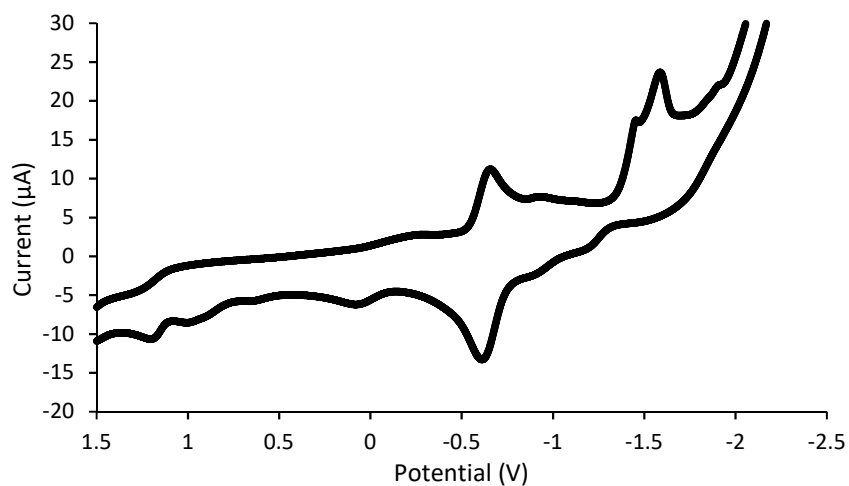


Figure A.139 Cyclic voltammogram of catalyst **14** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.633 V) versus Fc/Fc⁺.

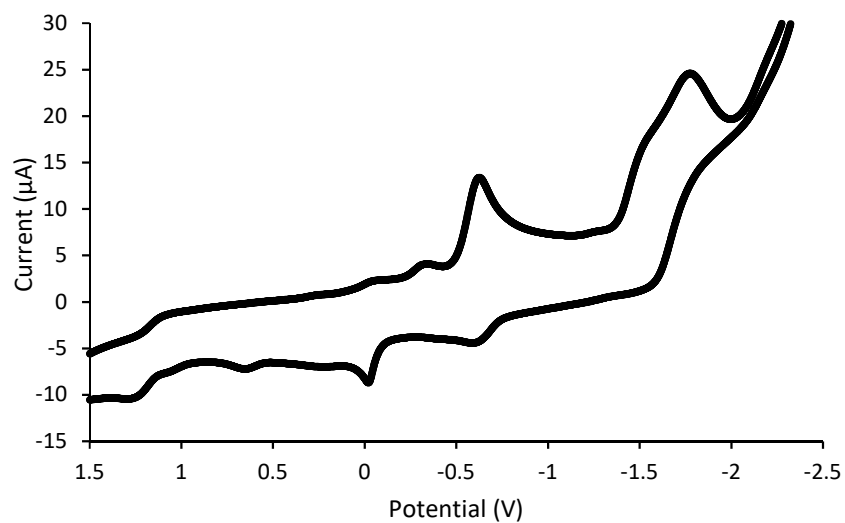


Figure A.140 Cyclic voltammogram of catalyst **15** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.605 V) versus Fc/Fc⁺.

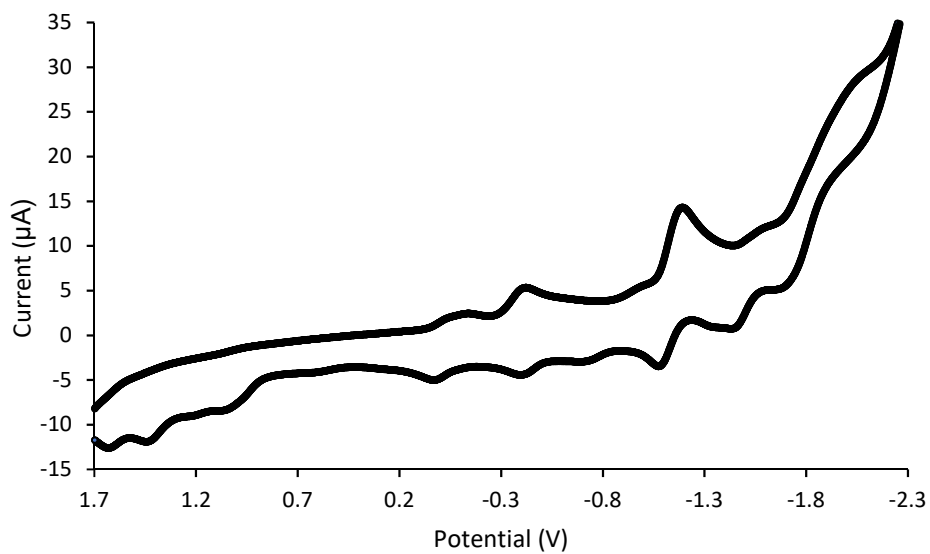


Figure A.141 Cyclic voltammogram of catalyst **16** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), versus Fc/Fc⁺.

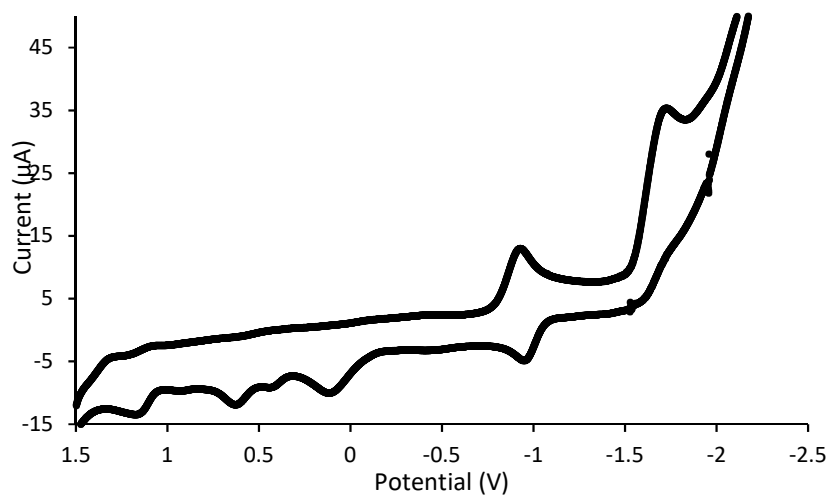


Figure A.142 Cyclic voltammogram of catalyst **17** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.936 V) versus Fc/Fc⁺.

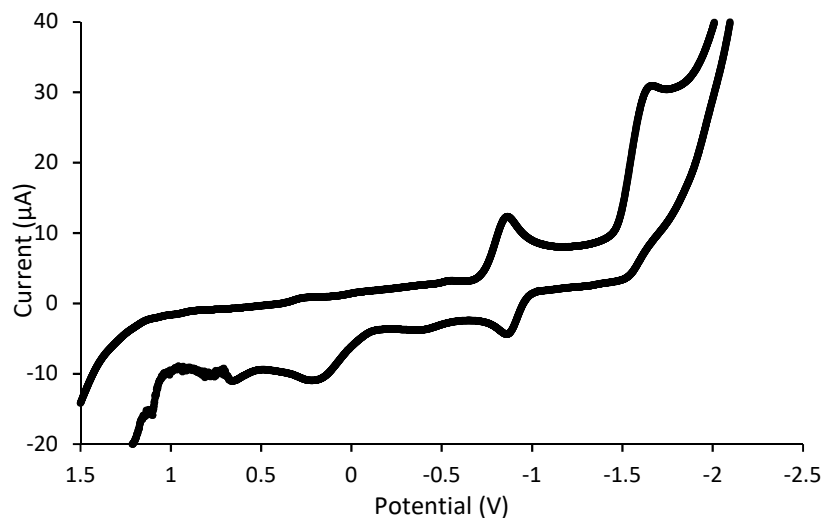


Figure A.143 Cyclic voltammogram of catalyst **18** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.862 V) versus Fc/Fc⁺.

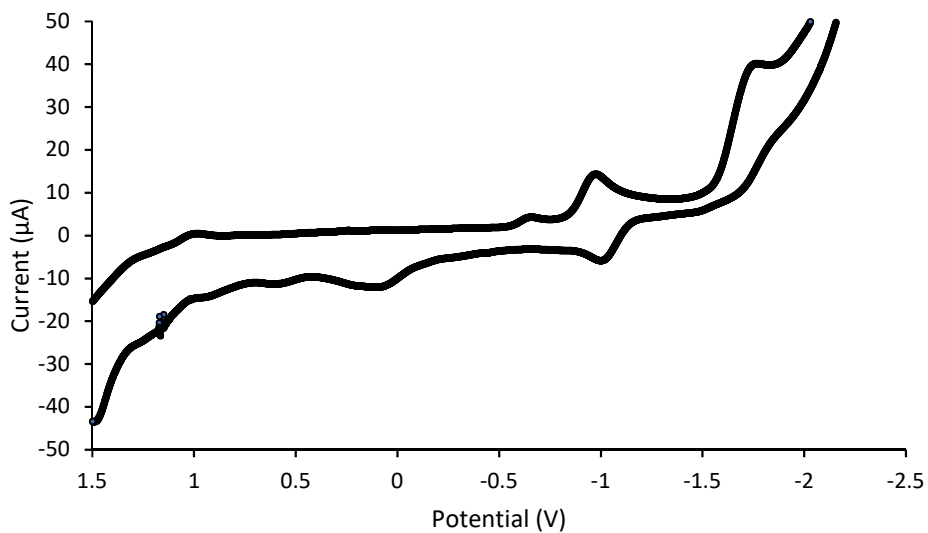


Figure A.144 Cyclic voltammogram of catalyst **19** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.987 V) versus Fc/Fc⁺.

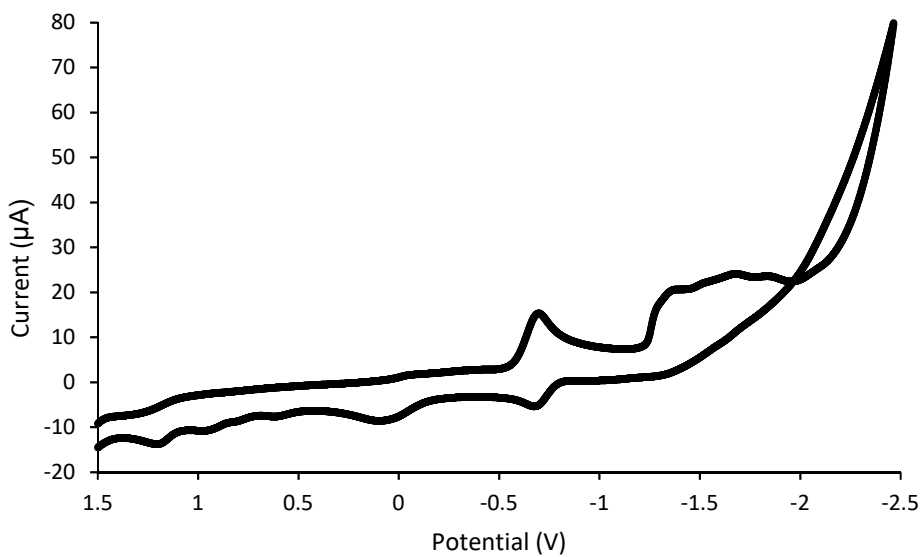


Figure A.145 Cyclic voltammogram of catalyst **20** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.686 V) versus Fc/Fc⁺.

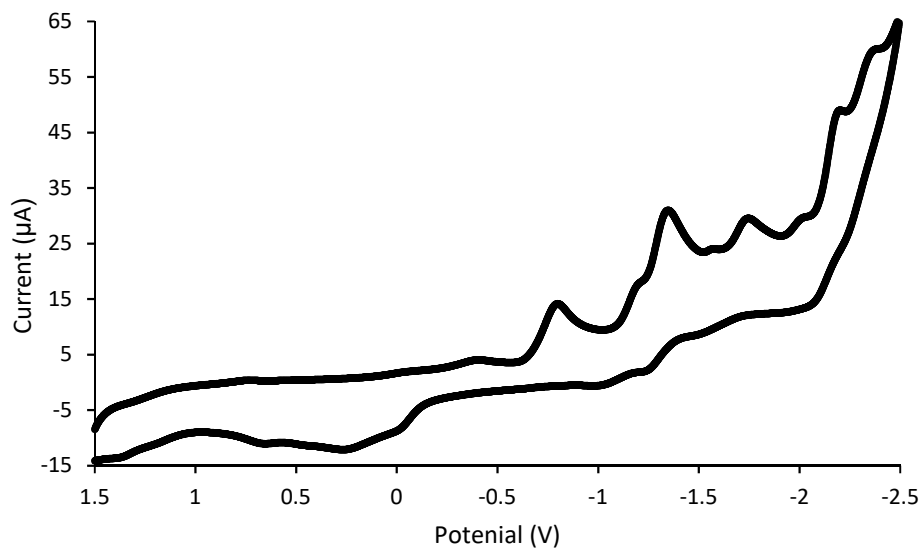


Figure A.146 Cyclic voltammogram of catalyst **21** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), ($E_{1/2}$ = -0.80 V) versus Fc/Fc⁺.

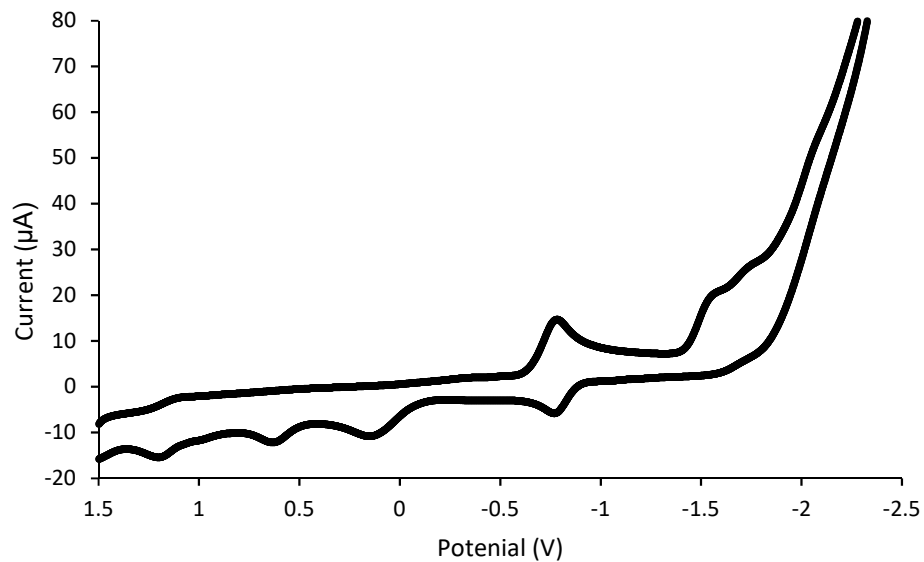


Figure A.147 Cyclic voltammogram of catalyst **22** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), ($E_{1/2}$ = -0.775 V) versus Fc/Fc⁺.

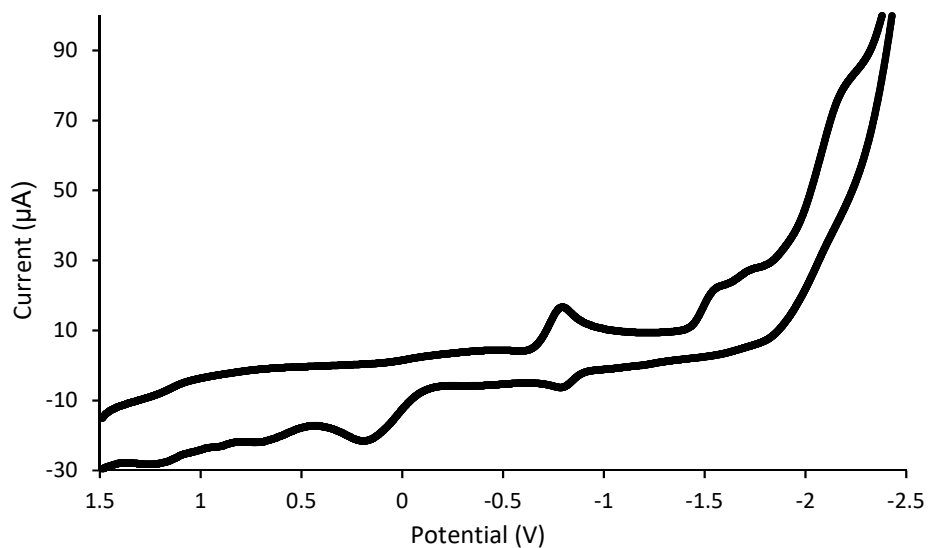


Figure A.148 Cyclic voltammogram of catalyst **23** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.791 V) versus Fc/Fc⁺.

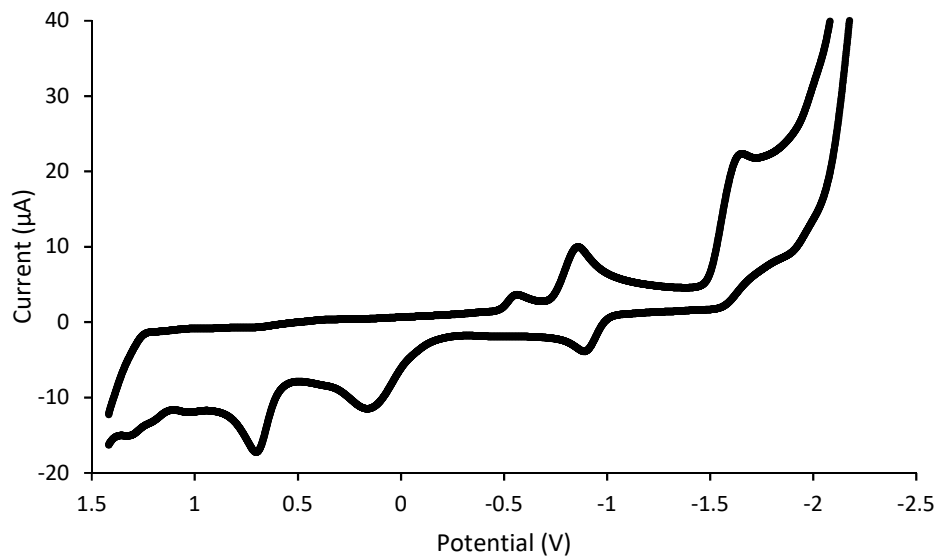


Figure A.149 Cyclic voltammogram of catalyst **24** (0.01 mmol) recorded at a scan rate of 100 mV/s in dichloromethane (5 mL), (*n*Bu)₄NPF₆ (0.20 M), (*E*_{1/2} = -0.874 V) versus Fc/Fc⁺.

A.6.3 X-Ray Crystallographic Data

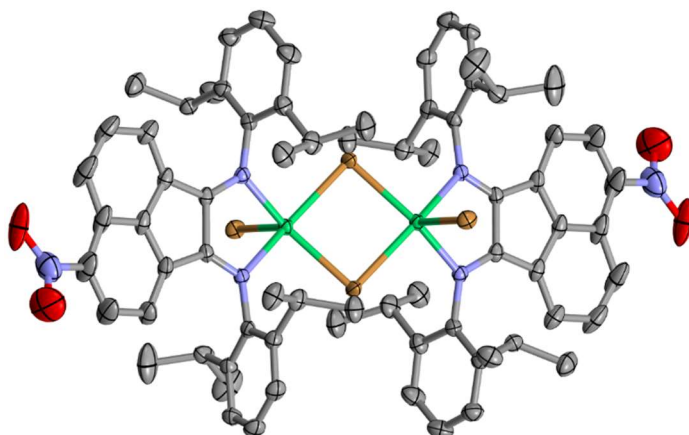


Figure A.150 ORTEP representation of **14** with thermal ellipsoids drawn at 50% probability. Hydrogens were omitted for clarity. X-ray quality single crystals of **14** were obtained by crystallization from DCM with pentanes via layering. Crystal data for $C_{72}H_{78}N_6O_4Br_4Ni_2$ (1528.46 g/mol); triclinic; space group P-1; $a = 10.0996(5)$ Å; $b = 11.8166(5)$ Å; $c = 16.4725(9)$ Å; $\alpha = 78.631(2)^\circ$; $\beta = 75.354(2)^\circ$; $\gamma = 80.217(2)^\circ$; $V = 1849.68(16)$ Å³; $Z = 1$; $T = 100(2)$ K; $\lambda = 0.71073$ Å; $\mu = 2.865$ mm⁻¹; $R_1 = 0.0530$; $wR_2 = 0.1459$ for 70274 reflections; GOF = 1.036.

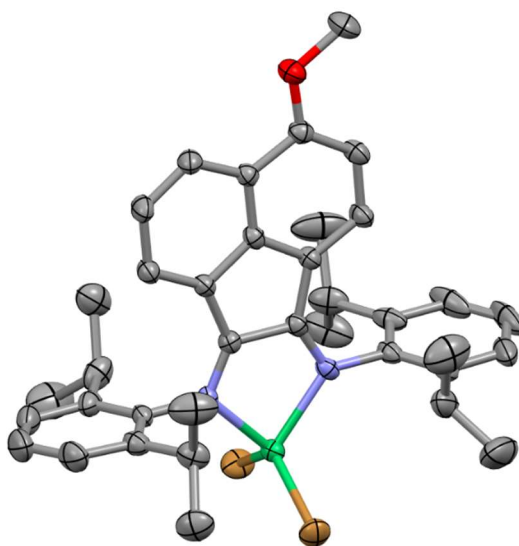


Figure A.151 ORTEP representation of **17** with thermal ellipsoids drawn at 50% probability. Hydrogens were omitted for clarity. X-ray quality single crystals of **17** were obtained by crystallization from DCM with pentane via layering. Crystal data for $C_{37}H_{42}N_2OBr_2Ni$ (749.26 g/mol); monoclinic; space group $P2_1/c$; $a = 23.509(5)$ Å; $b = 17.533(3)$ Å; $c = 18.107(4)$ Å; $\alpha = 90^\circ$; $\beta = 94.937(8)^\circ$; $\gamma = 90^\circ$; $V = 7436(3)$ Å³; $Z = 4$; $T = 100(2)$ K; $\lambda = 0.71073$ Å; $\mu = 2.773$ mm⁻¹; $R_1 = 0.0673$; $wR_2 = 0.1659$ for 196966 reflections; GOF = 1.053.

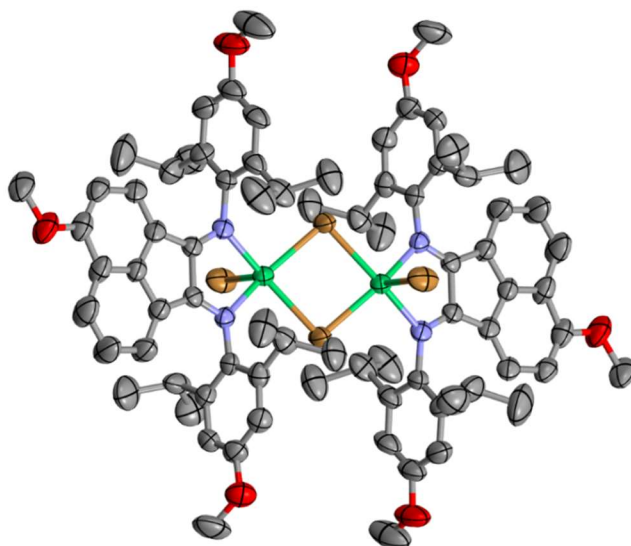


Figure A.152 ORTEP representation of **19** with thermal ellipsoids drawn at 50% probability. Hydrogens were omitted for clarity. X-ray quality single crystals of **19** were obtained by crystallization from DCM with pentane via vapor diffusion. Crystal data for $C_{78}H_{92}N_4O_6Br_4Ni_2$ (1618.62 g/mol); monoclinic; space group $P2_1/n$; $a = 12.912(4)$ Å; $b = 17.175(5)$ Å; $c = 19.567(6)$ Å; $\alpha = 90^\circ$; $\beta = 90.610(12)^\circ$; $\gamma = 90^\circ$; $V = 4339(2)$ Å³; $Z = 4$; $T = 117(2)$ K; $\lambda = 0.71073$ Å; $\mu = 2.330$ mm⁻¹; $R_1 = 0.0850$; $wR_2 = 0.2417$ for 104250 reflections; GOF = 1.036.

A.6.4 GPC Traces

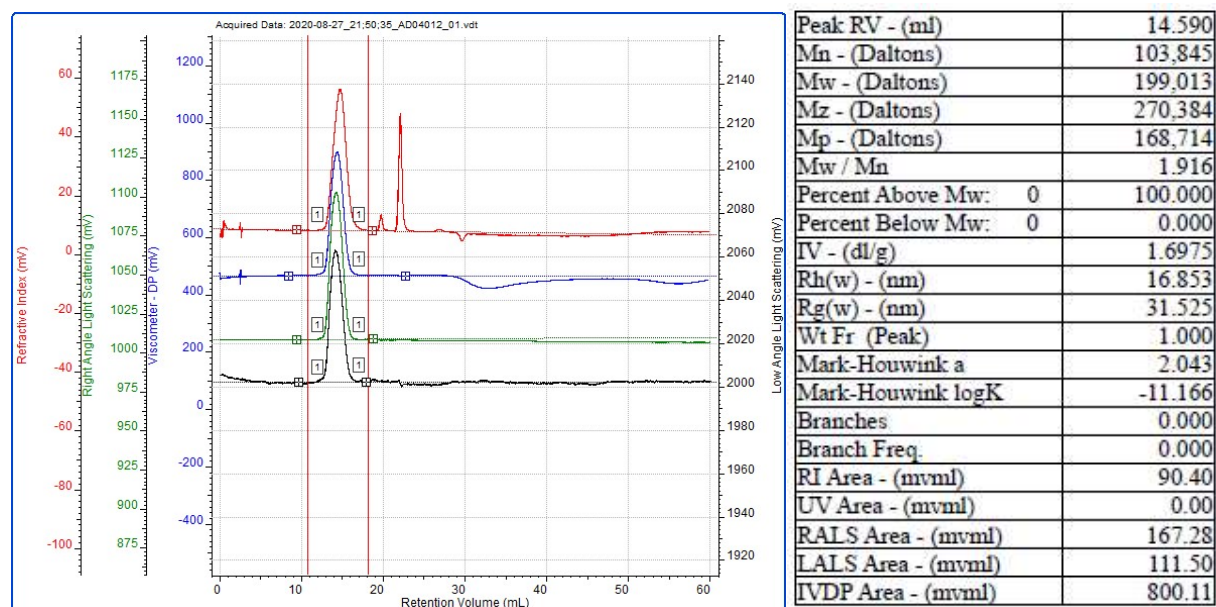


Figure A.153 GPC trace of PLA obtained using **13**. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table S.1, Entry 1).

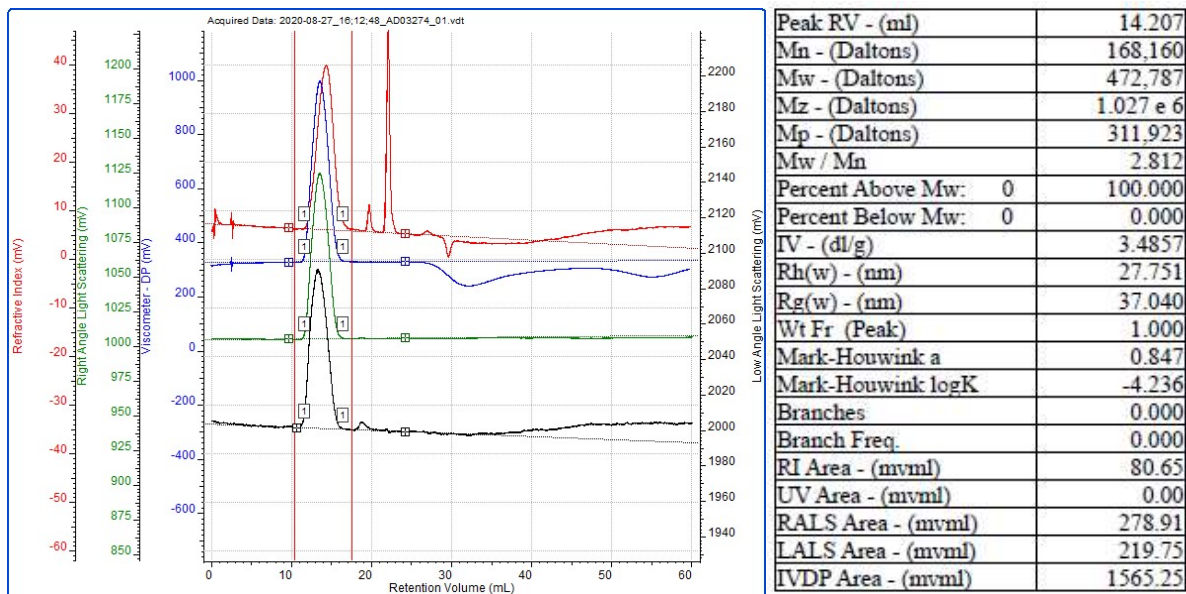


Figure A.154 GPC trace of PLA obtained using 14. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.1, Entry 2).

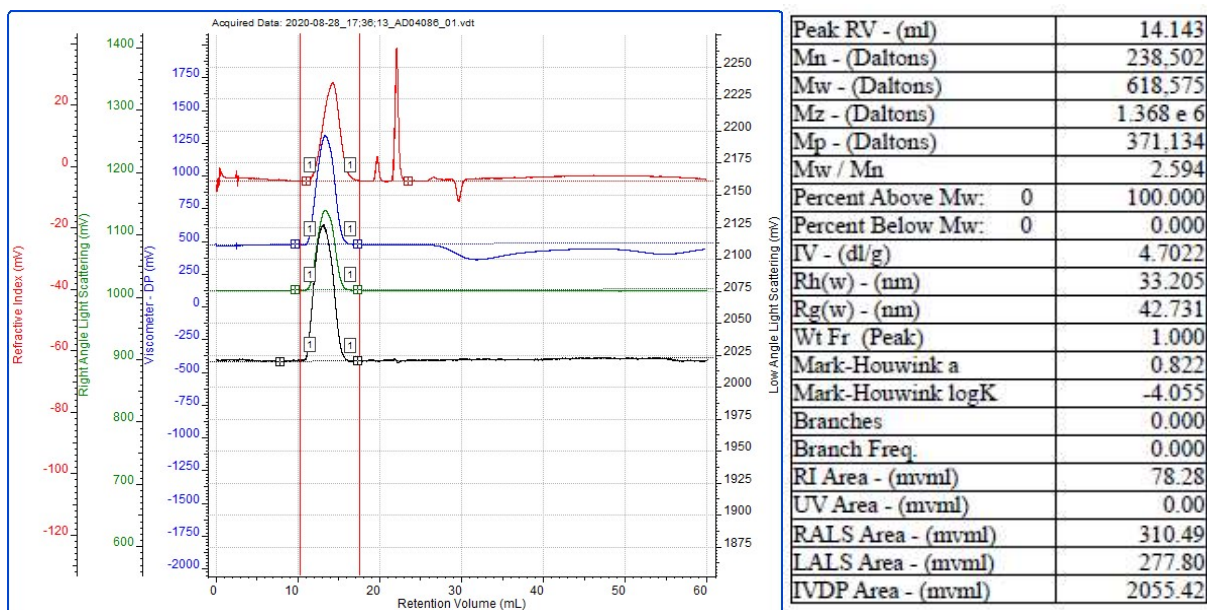


Figure A.155 GPC trace of PLA obtained using 15. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.1, Entry 3).

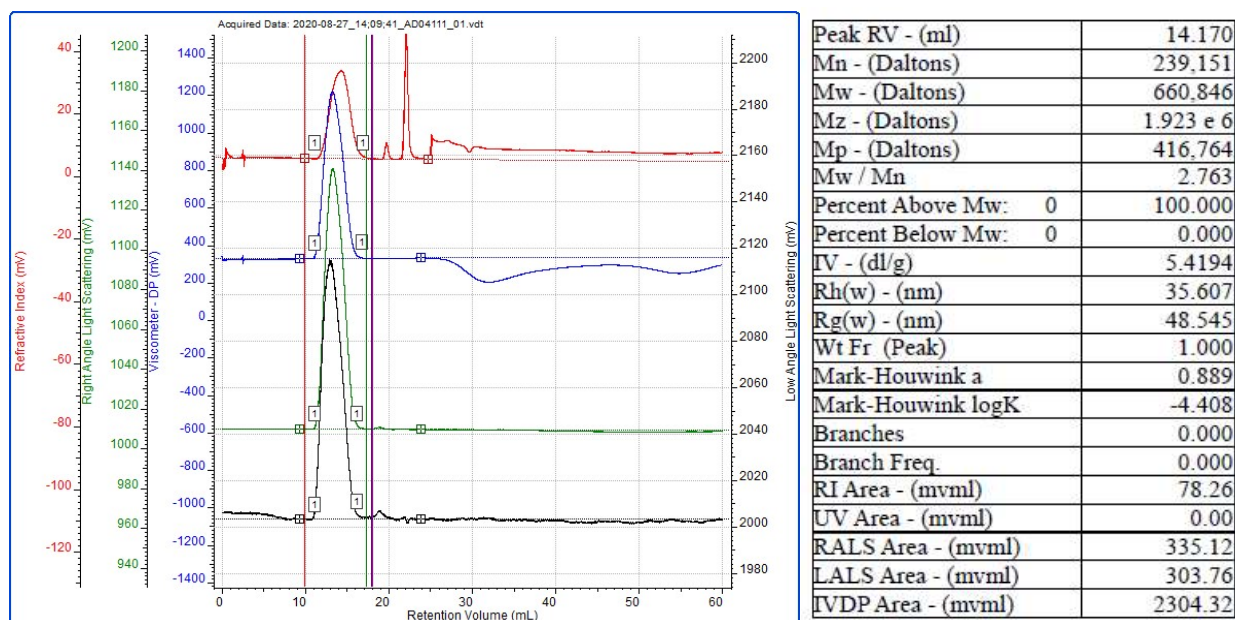


Figure A.156 GPC trace of PLA obtained using 16. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.1, Entry 4).

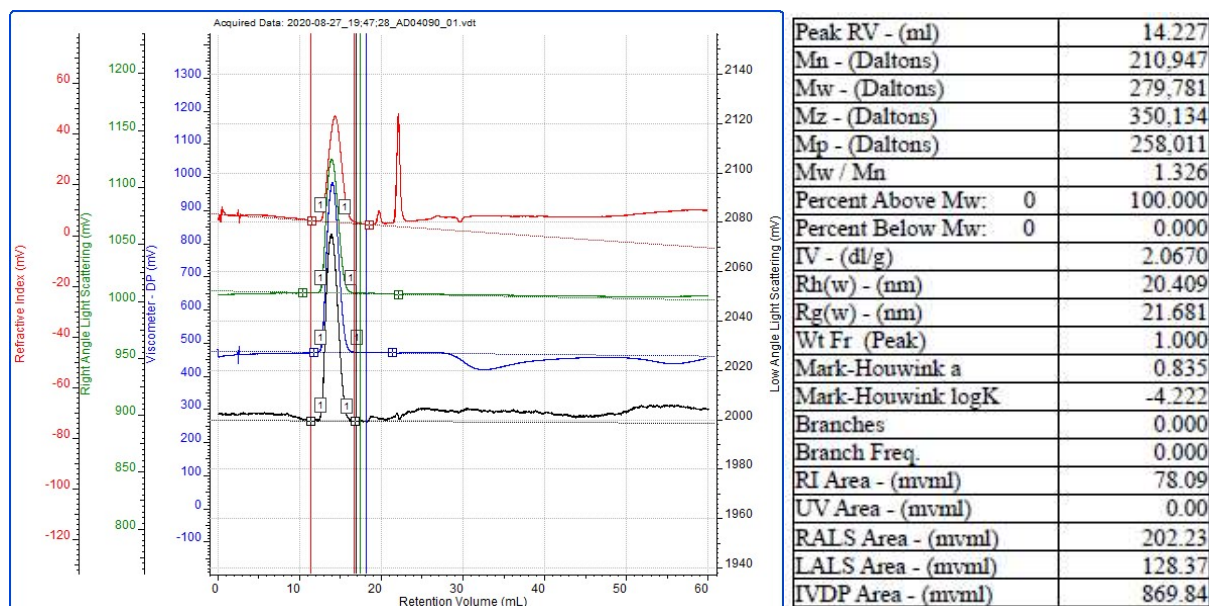


Figure A.157 GPC trace of PLA obtained using 17. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.1, Entry 5).

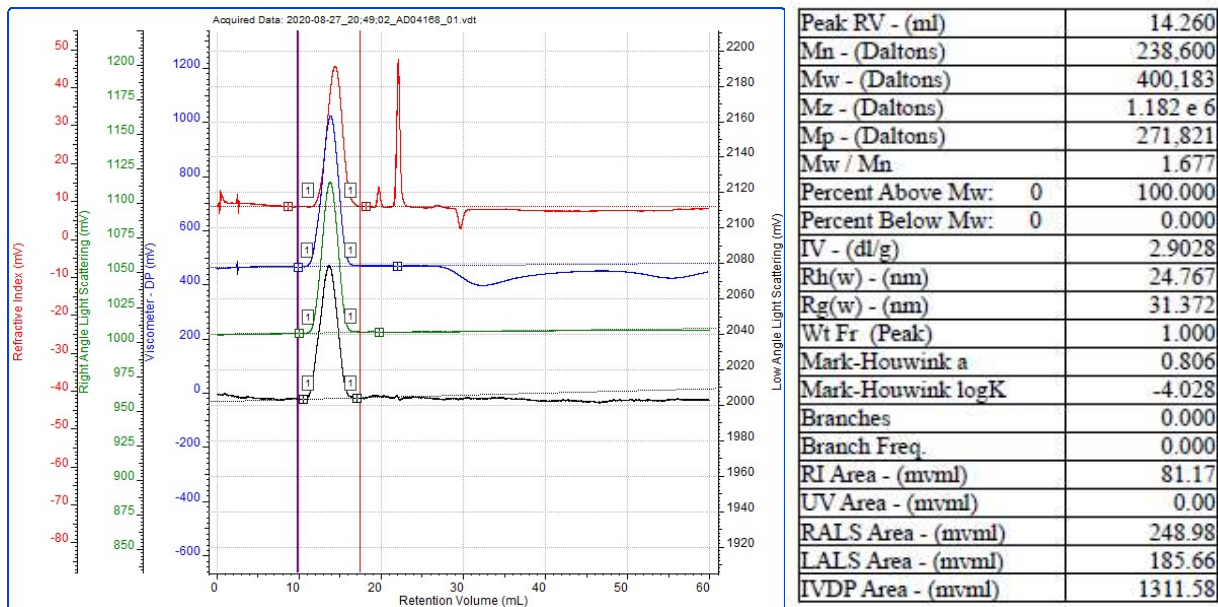


Figure A.158 GPC trace of PLA obtained using 18. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.1, Entry 6).

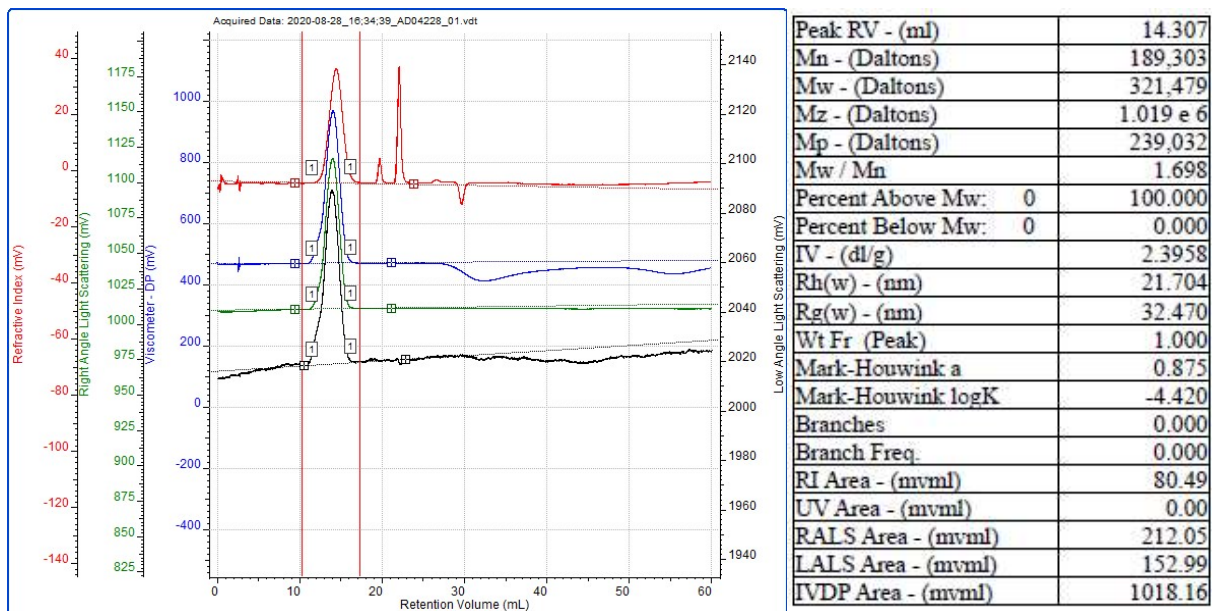


Figure A.159 GPC trace of PLA obtained using 19. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.1, Entry 7).

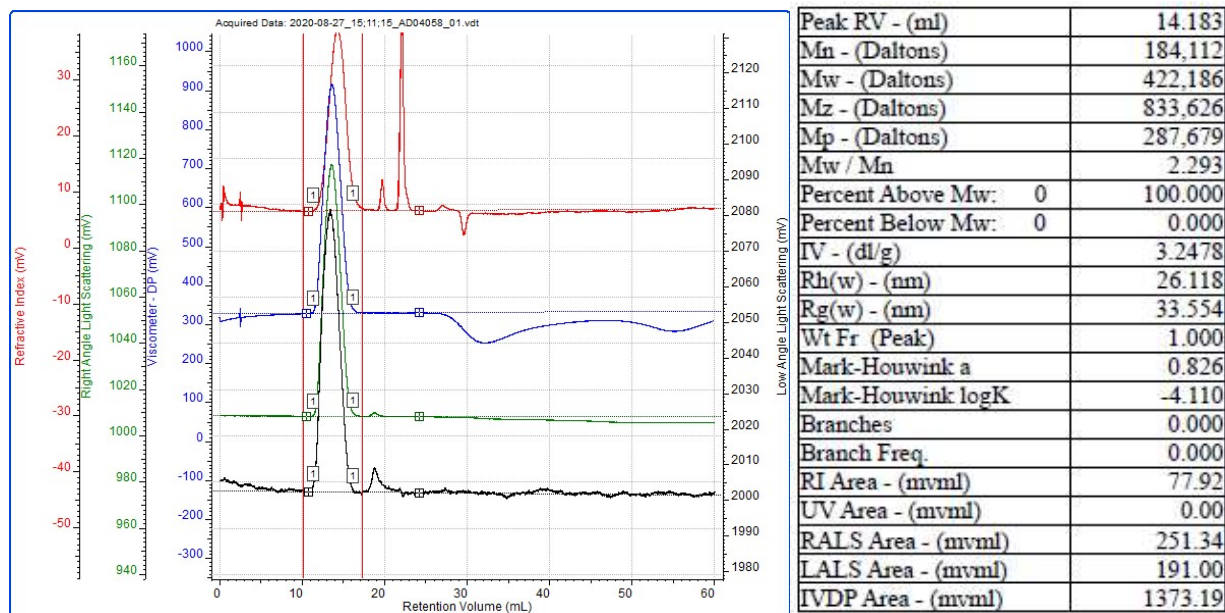


Figure A.160 GPC trace of PLA obtained using 20. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.2, Entry 1).

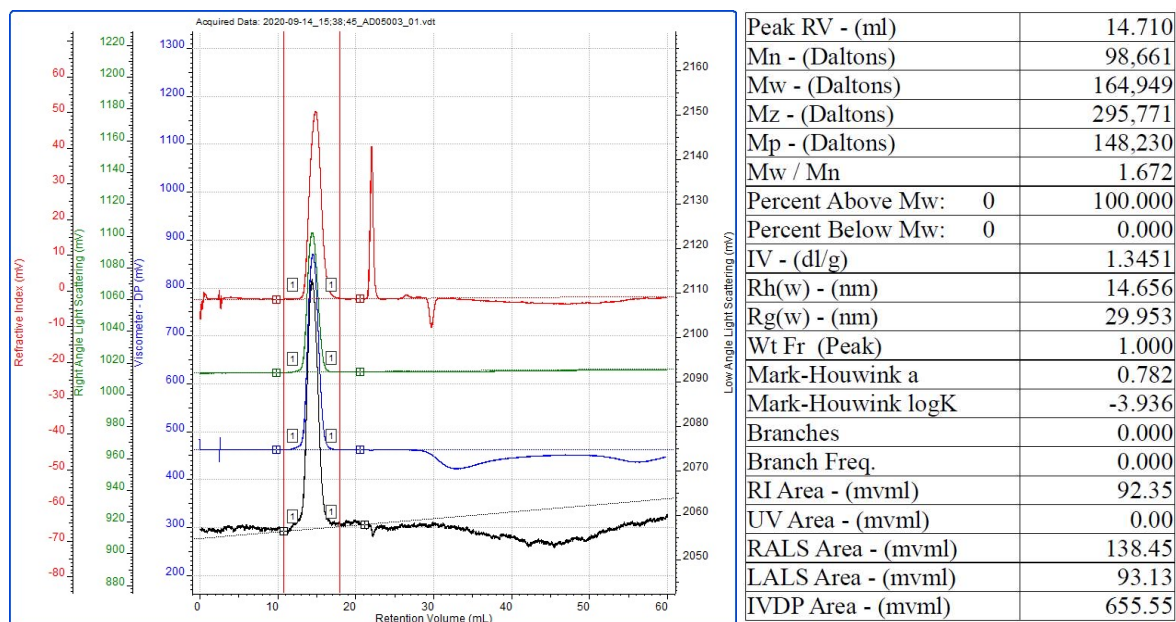


Figure A.161 GPC trace of PLA obtained using 21. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.2, Entry 2).

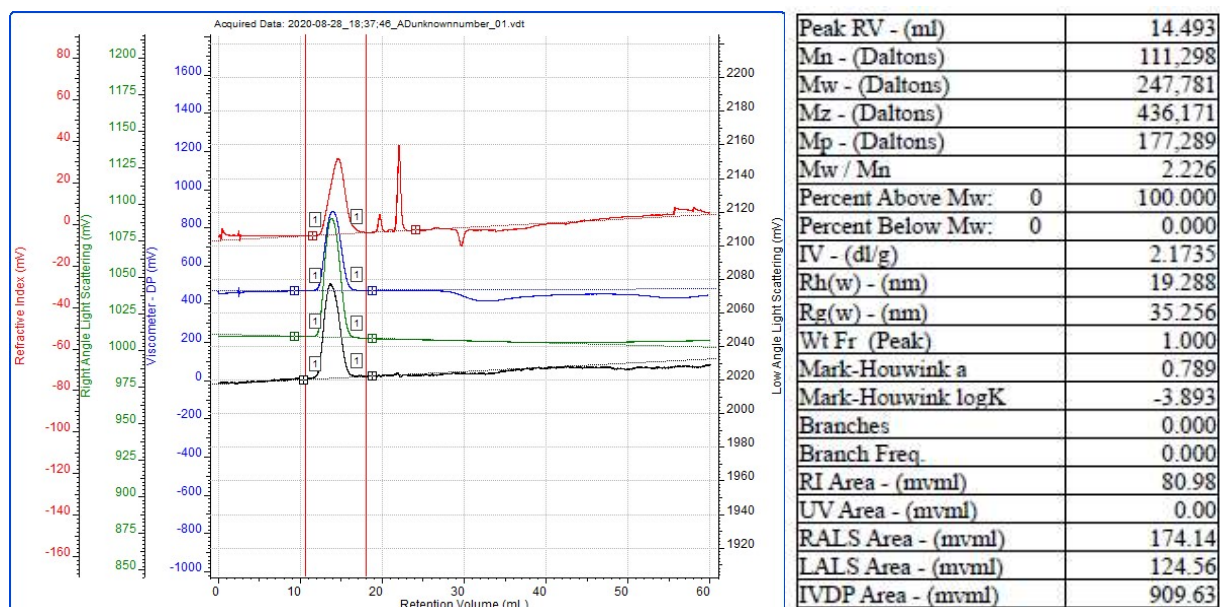


Figure A.162 GPC trace of PLA obtained using 22. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.2, Entry 3).

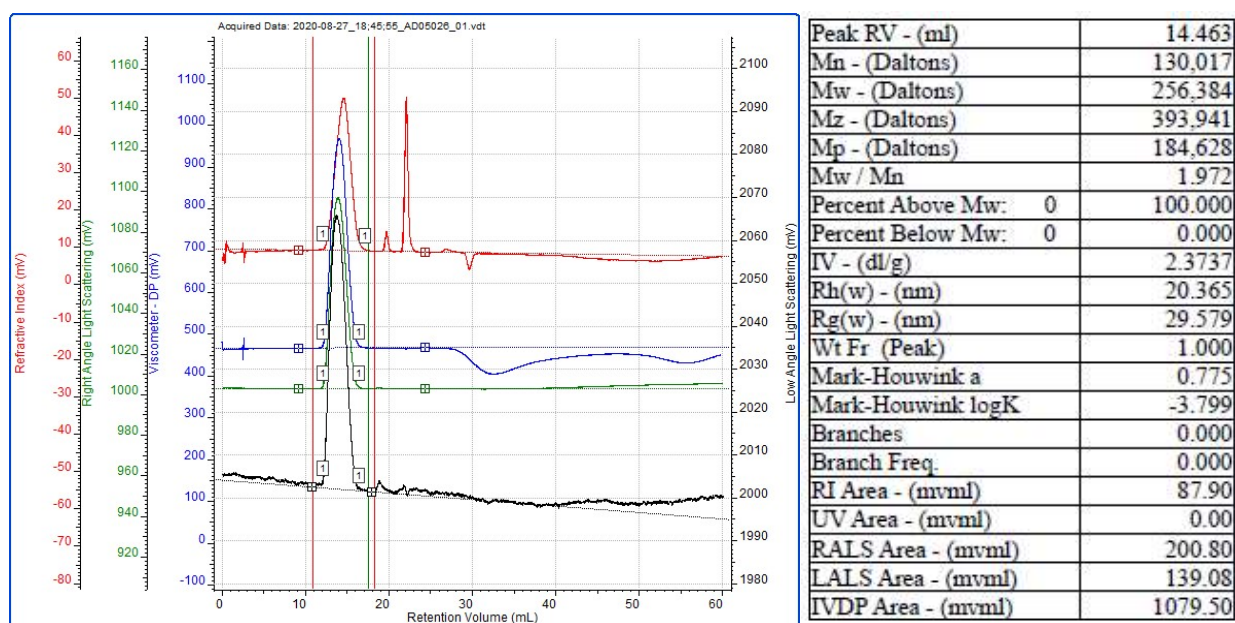


Figure A.163 GPC trace of PLA obtained using 23. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.2, Entry 4).

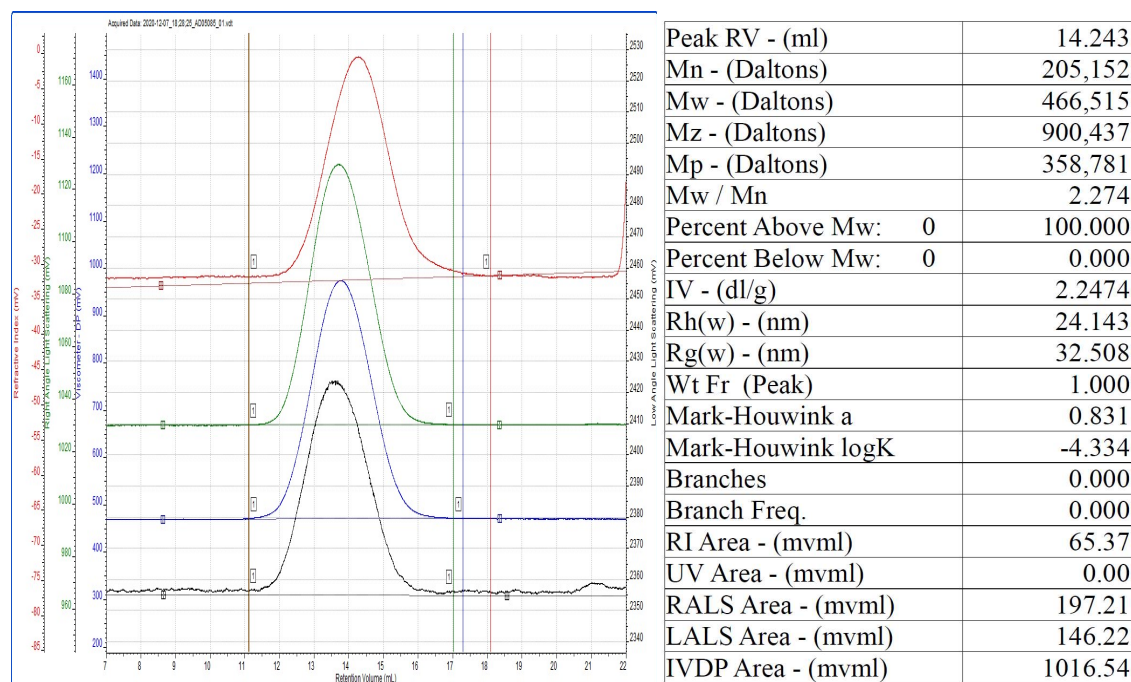


Figure A.164 GPC trace of PLA obtained using **24**. Samples measured in THF at 30 °C and reported as absolute molecular weights (Table 5.2, Entry 5).

A.6.5 Differential Scanning Calorimetry

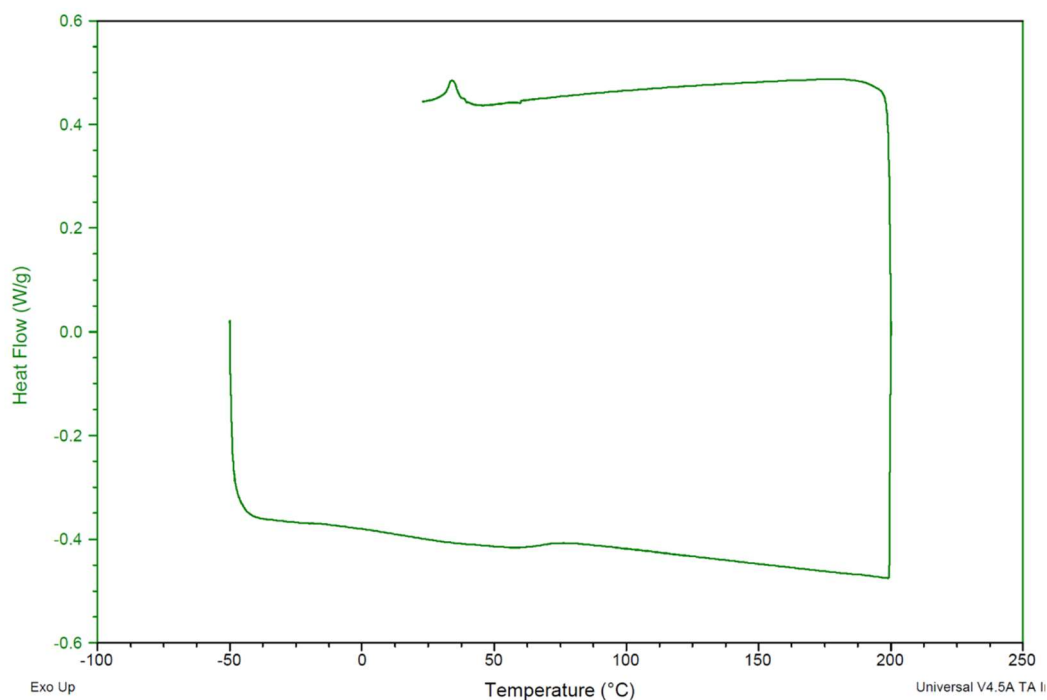


Figure A.165 Representative DSC of PE produced using **13**.

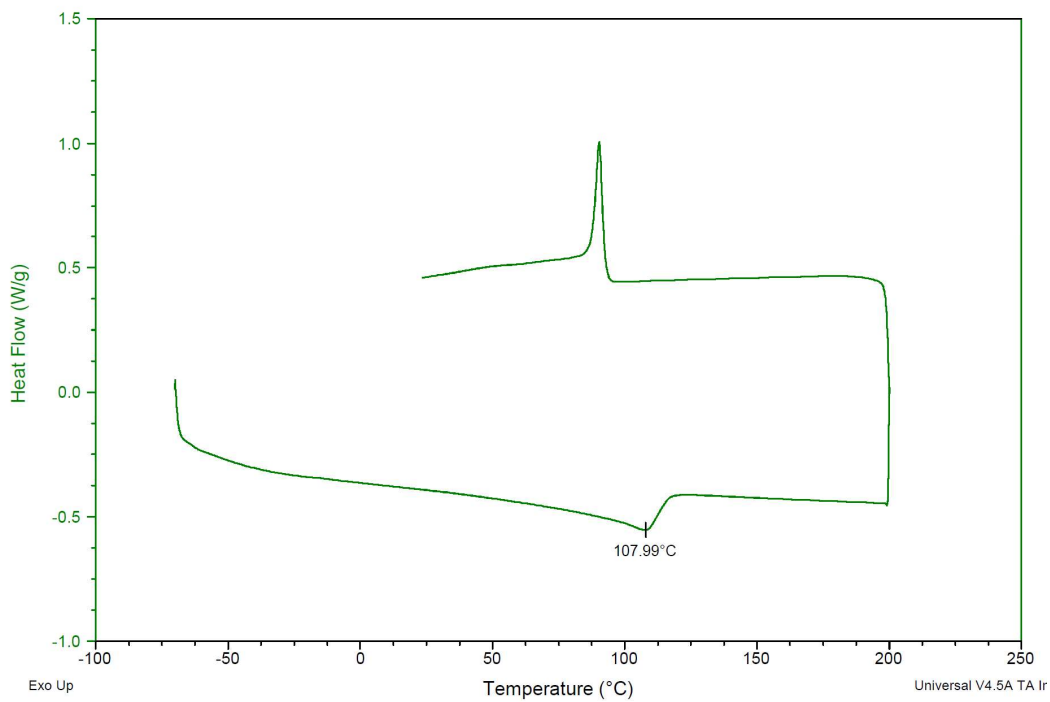


Figure A.166 Representative DSC of PE produced using **14**.

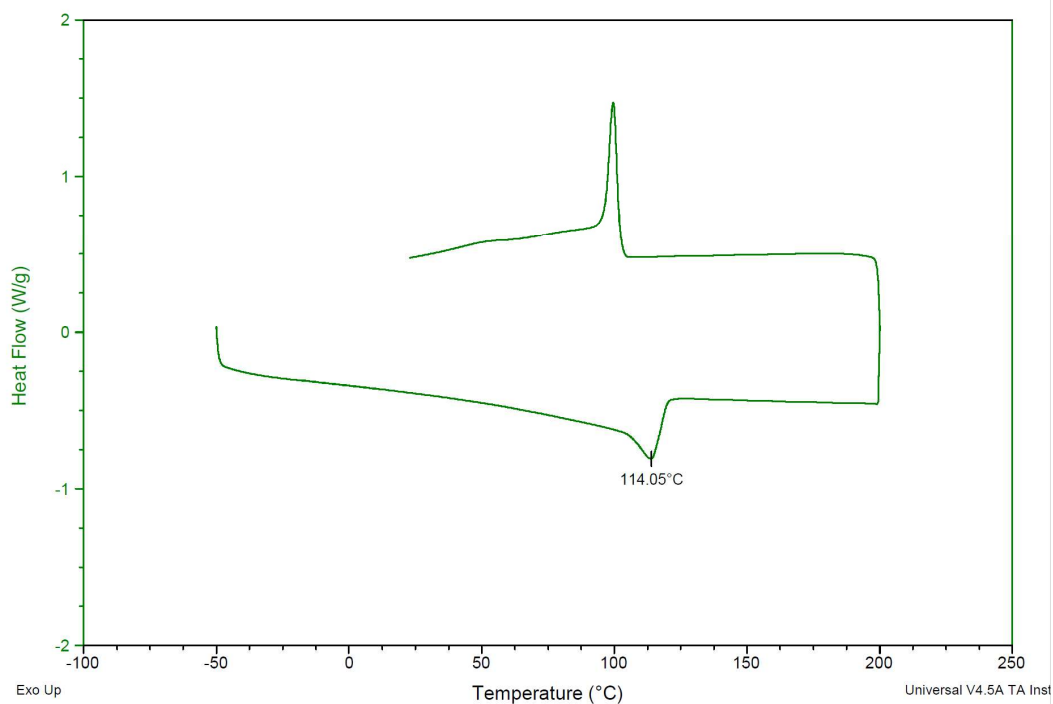


Figure A.167 Representative DSC of PE produced using **15**.

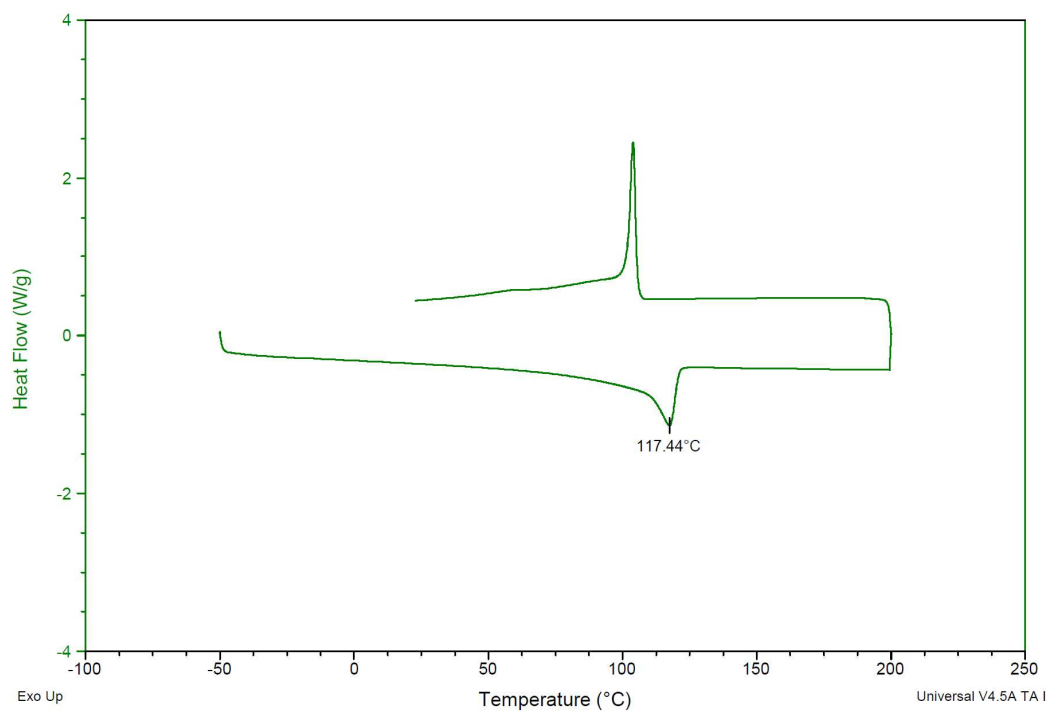


Figure A.168 Representative DSC of PE produced using **16**.

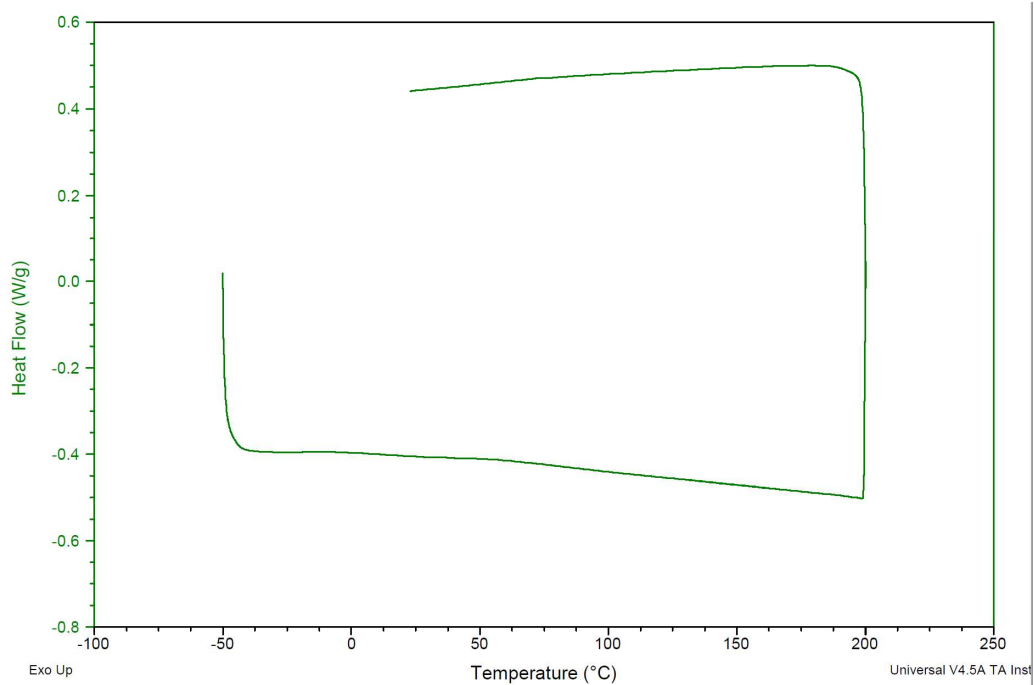


Figure A.169 Representative DSC of PE produced using **17**.

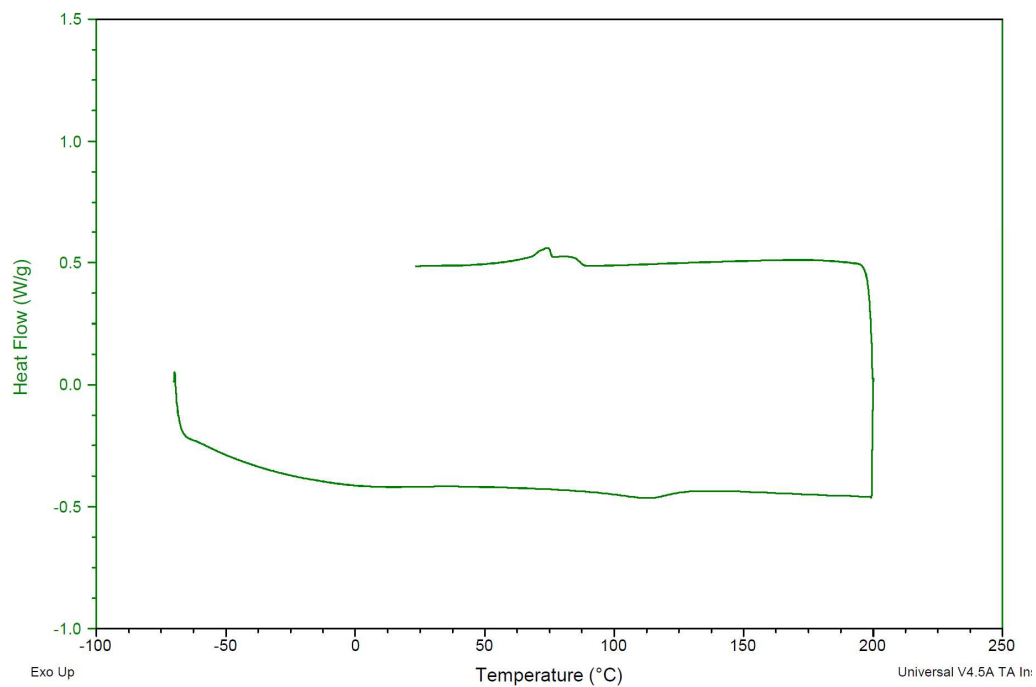


Figure A.170 Representative DSC of PE produced using 18.

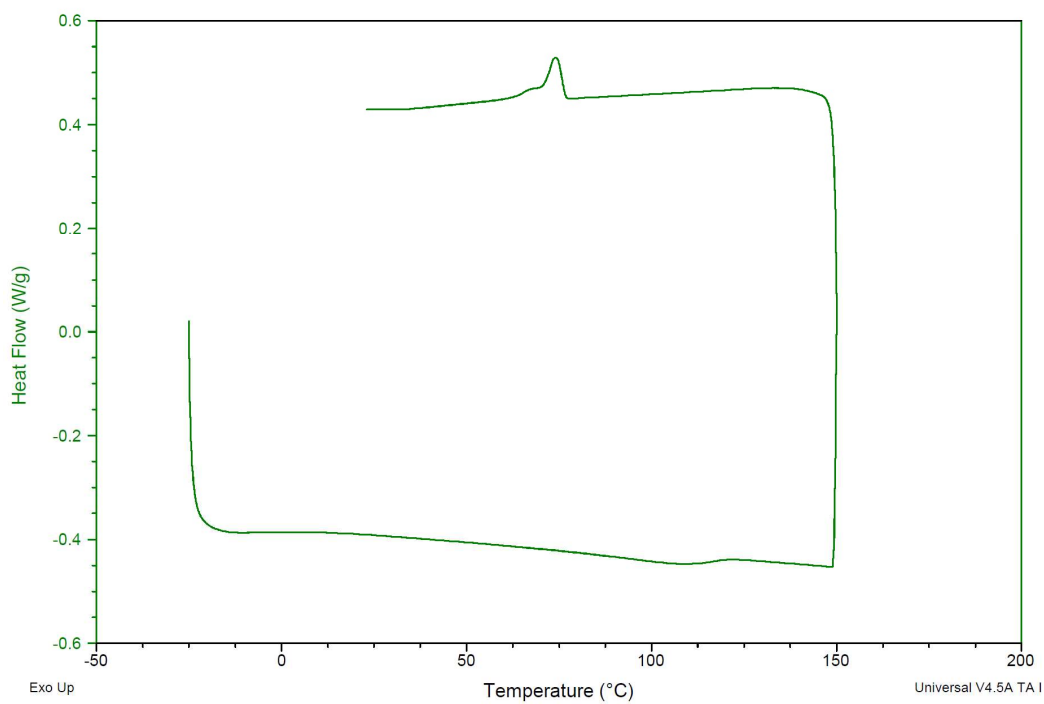


Figure A.171 Representative DSC of PE produced using 19.

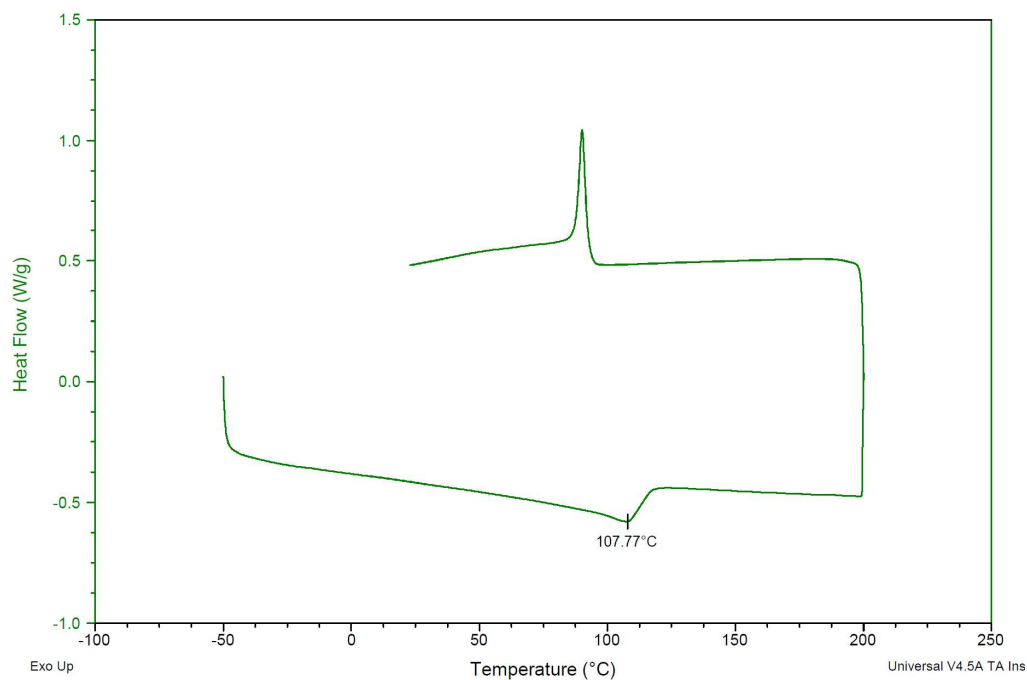


Figure A.172 Representative DSC of PE produced using 20.

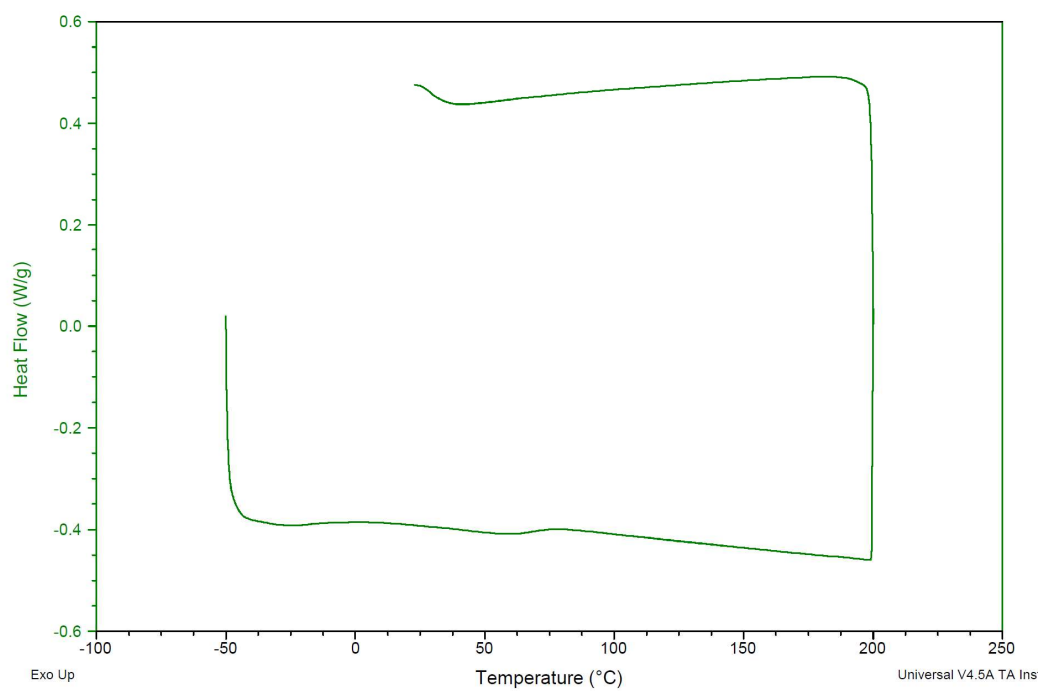


Figure A.173 Representative DSC of PE produced using 21.

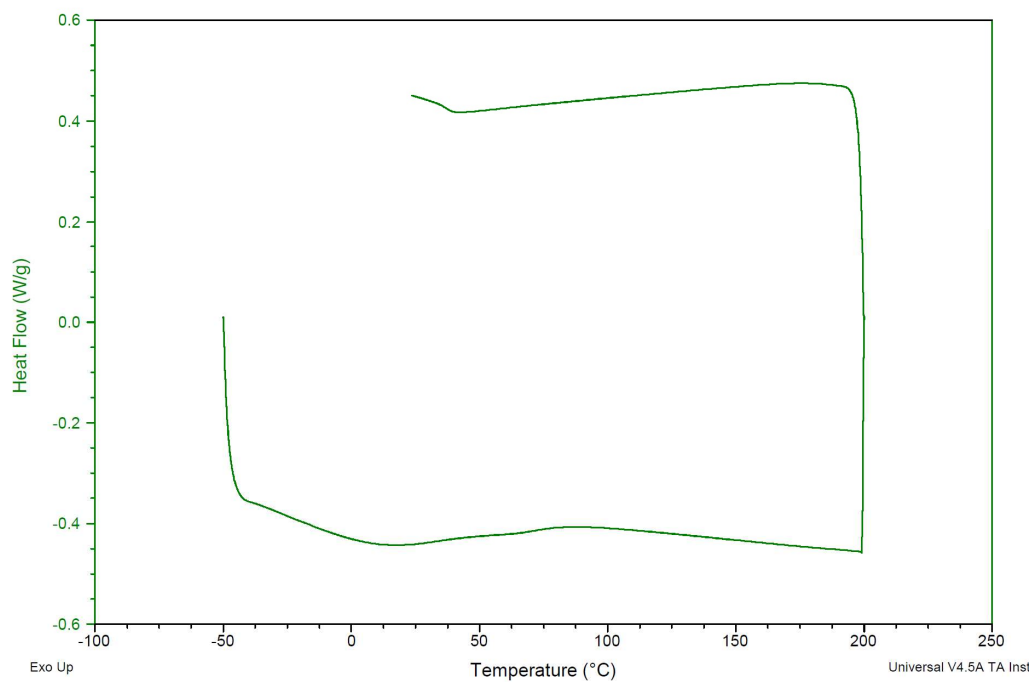


Figure A.174 Representative DSC of PE produced using 22.

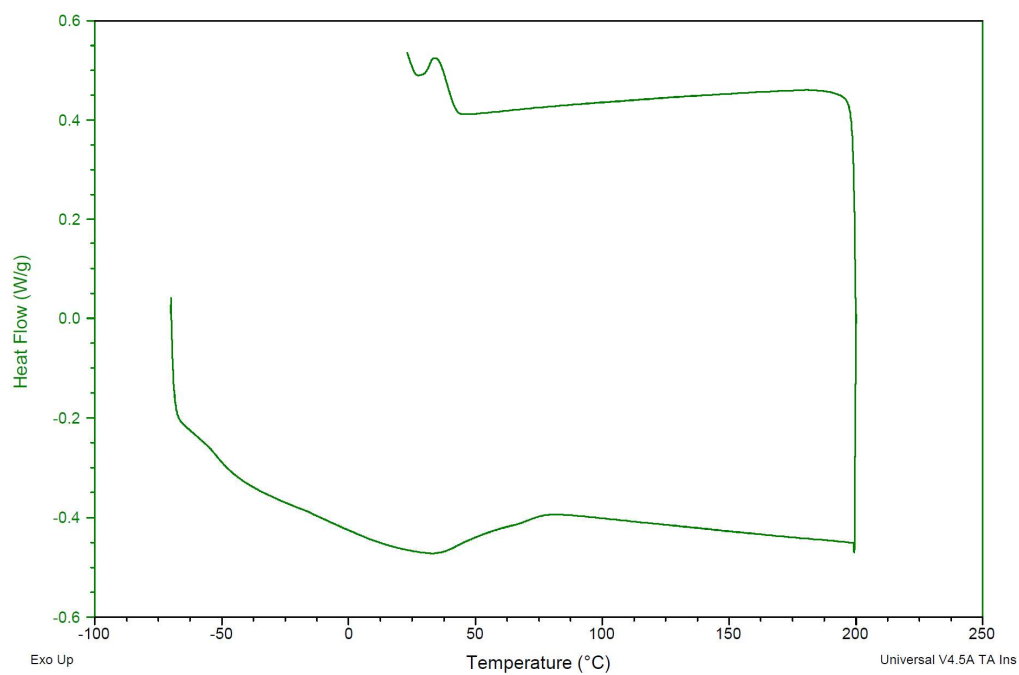


Figure A.175 Representative DSC of PE produced using 23.

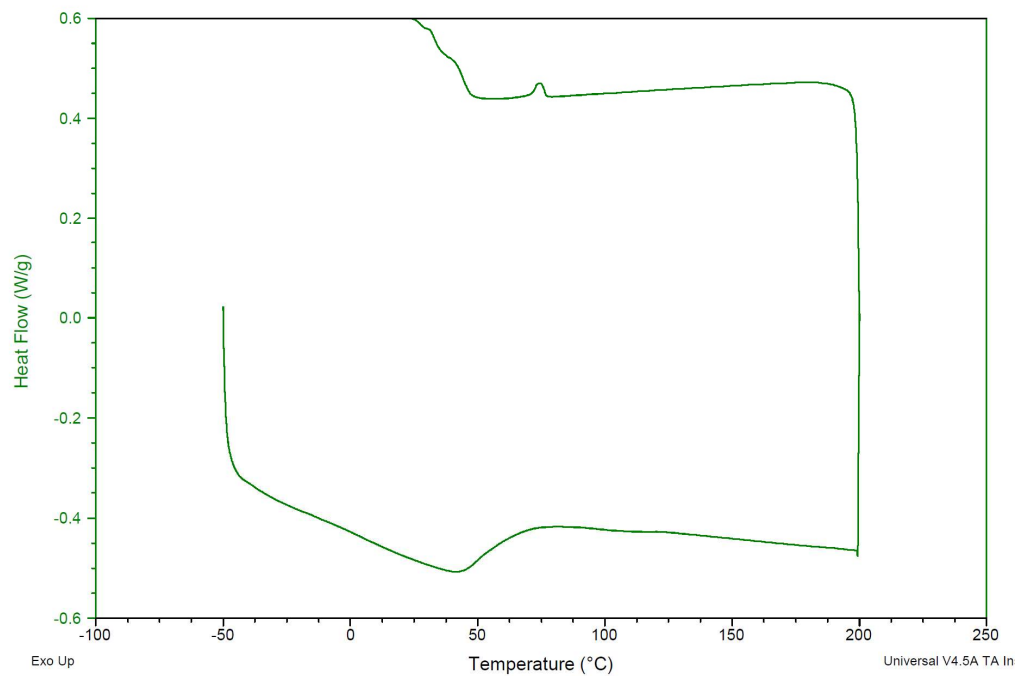


Figure A.176 Representative DSC of PE produced using **24**.

A.6.6 Computation of Theoretical Branching Content

In the Roy groups previous work,¹⁹⁵ we computed the catalytic reaction pathway shown in **Scheme 5.2** using DFT, and determined that the branching density (B = number of branches per 1000 carbons) was dictated by the equilibrium between **I-3^{n-pr}** and **I-3^{i-pr}**, rather than by the kinetic competition between the second ethylene coordination from **I-2^{n-pr}** to **I-3^{n-pr}** versus the second ethylene coordination from **I-2^{i-pr}** to **I-3^{i-pr}**. Therefore, in the present work, we calculated $\Delta G = G(\text{I-3}^{i\text{-pr}}) - G(\text{I-3}^{n\text{-pr}})$ using the DFT method described in the main text, and subsequently calculated the equilibrium constant, K_{eq} , and B at $T = 298.15$ K for catalysts **13-19** using the following equations, where R is the molar gas constant.

$$K_{eq} = \frac{\text{conc. of I-3}^{i\text{-pr}}}{\text{conc. of I-3}^{n\text{-pr}}} = \exp\left(\frac{-\Delta G}{RT}\right)$$
$$B = \frac{\text{conc. of I-3}^{i\text{-pr}} \times 1000}{\text{total conc. of I-3}^{n\text{-pr}} \text{ and I-3}^{i\text{-pr}}} = \left(\frac{1}{K_{eq} + 1}\right) \times 1000$$

Table A.1: Computed values of ΔG , K_{eq} , B , Ni-H β distance in **I-3^{i-pr}**, Ni-ethylene distance in **I-3^{i-pr}**, and Ni-ethylene distance in **I-3^{n-pr}** for catalysts **13-19**, corresponding to **Figure 5.4** in the main text.

Catalyst	ΔG (kcal/mol)	K_{eq} at 298.15 K	B at 298.15 K	Ni-H β distance in I-3^{i-pr} (Å)	Ni- ethylene distance in I-3^{i-pr} (Å)	Ni-ethylene distance in I-3^{n-pr} (Å)
13	+1.158	0.141	123.98	1.883	2.011	2.048
14	+2.188	0.025	24.30	1.907	2.009	2.038
15	+3.290	0.004	3.86	1.903	2.010	2.036
16	+3.188	0.005	4.57	1.900	2.010	2.036
17	+0.960	0.198	165.07	1.884	2.008	2.047
18	+1.398	0.094	86.26	1.882	2.008	2.047
19	+0.755	0.279	218.46	1.886	2.008	2.047

A.7 Experimental – Chapter 6

A.7.1 General Methods and Materials.

THF was purified using a two-column purification system and degassed *via* freeze-pump-thaw (x3). Triethylamine was purified by distillation off of CaH₂ and degassed *via* freeze-pump-thaw (x3). All NMR solvents were purchased from Cambridge Isotope Laboratories. ¹H NMR spectra were recorded on a Varian 300 MHz spectrometer. Chemical shifts are reported with respect to solvent residual peak, 7.26 (CDCl₃). Acetylferrocene was purchased from Fisher Scientific and purified by silica gel plug using 90:10 hexanes: ethyl acetate as an eluent prior to use. All other reagents were used as received.

A.7.2 Synthesis of 2-adamantyl-4-iodohydroxybenzene (**28**)

To a round bottom flask was added 4-iodophenol (5.0 g, 22.7 mmol), 1-adamantanol (3.470 g, 22.7 mmol), and DCM (15 mL). A H₂SO₄: acetic acid (1.5 mL: 6.5 mL) solution was slowly added and the reaction was stirred for 2 days. The reaction was then diluted with water, neutralized with saturated NaHCO₃ solution, extracted with DCM, and wash with water. The organic layer was dried with NaSO₄, filtered, and the crude product was

purified by silica gel flash column chromatography using 95:5 hexanes: ethyl acetate as an eluent to yield **28** (3.92 g, 11.1 mmol, 49%). All characterization matched previously reported literature.

A.7.3 Synthesis of 3-adamantyl-2-hydroxy-5-iodo-benzaldehyde (**29**)

In a glove box, paraformaldehyde (0.185 g, 6.16 mmol), MgCl_2 (0.533 g, 5.6 mmol), and THF (3 mL) were added to a pressure flask. Triethylamine (0.8 mL, 5.6 mmol) was added followed by **28** (1.00 g, 2.8 mmol) in THF (7 mL). The reaction was stirred at 80 °C overnight. The reaction was cooled to room temperature, diluted with chloroform (60 mL), water (50 mL), and 1 M HCl (3 mL) then stirred overnight. The organic layer was then extracted, washed with water followed by brine. All volatiles were removed under reduced pressure and the crude product was purified by silica gel flash column chromatography using 95:5 hexanes: ethyl acetate as an eluent to yield **29** (0.60 g, 1.56 mmol, 55%). All characterization matched previously reported literature.

A.7.4 Synthesis of 3-adamantyl-5-ethynylferrocene-2-hydroxybenzaldehyde (**30**)

To a Schlenk flask was added **29** (3.0 g, 7.85 mmol), ethynyl ferrocene (1.813 g, 8.63 mmol), and THF (40 mL). To a second Schlenk flask was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.551 g, 0.785 mmol) and CuI (0.037 g, 0.196 mmol). The ethynyl ferrocene solution was added to the [Pd] Schlenk flask via cannula followed by Hunig's base (2.8 mL) via syringe. The reaction was stirred for 36 h. All volatiles were removed under vacuum. The crude product was purified via celite/silica gel plug using a gradient eluent system (100 hexanes to 90:10 hexanes:DCM to 80:20 hexanes:DCM) to yield **30** as an orange solid (1.7685 g, 3.80 mmol, 82%). ^1H NMR (CDCl_3), δ , ppm: 1.83 (s, 6H, Ad), 2.15 (s, 9H, Ad), 4.26 (s, 7H, Cp), 4.51 (t, 2H, Cp), 7.55 (d, 2H, aromatic), 9.85 (s, 1H, aldehyde), 11.91 (s, 1H, OH).

A.7.5 Synthesis of $\text{C}_{60}\text{H}_{60}\text{N}_2\text{O}_2\text{Fe}_2$ (**31**)

To a round bottom flask was added **30** (2.0 g, 4.3 mmol), ethanol (30 mL), ethylenediamine (0.14 mL, 2.14 mmol), and 10 drops formic acid. The reaction was stirred at reflux for 4 h, cooled to room temperature, filtered, and washed with ethanol to yield **31** as an orange solid (1.84 g, 1.9 mmol, 89%) ^1H NMR (CDCl_3), δ , ppm: 1.79 (s, 12H, Ad) 2.10 (s, 8H, Ad), 2.17 (s, 10H, Ad), 3.95 (s, 4H, CH_2), 4.23 (s, 14H, Cp), 4.47 (s, 4H, Cp), 7.26 (s, 2H, aromatic), 7.37 (s, 2H, aromatic), 8.36 (s, 2H, NCH_2).

A.7.6 Synthesis of $\text{C}_{60}\text{H}_{64}\text{N}_2\text{O}_2\text{Fe}_2$ (**32**)

To a round bottom flask was added **31** (1.5 g, 1.57 mmol), 50:50 THF: MeOH (60 mL), and excess NaBH_4 . The reaction was stirred overnight, followed by removal of solvent under reduced pressure. The reaction was extracted with DCM, washed with water, dried with NaSO_4 , and filtered to **32** as an orange solid (1.459 g, 1.52 mmol, 97%). ^1H NMR (CDCl_3), δ , ppm: 1.78 (s, 12H, Ad), 2.07 (s, 8H, Ad), 2.14 (s, 10H, Ad), 2.84 (s, 4H, CH_2), 3.96 (s, 4H, CH_2), 4.20 (t, 4H, Cp), 4.23 (s, 10H, Cp), 4.46 (t, 4H, Cp), 7.00 (s, 2H, aromatic), 7.28 (s, 2H, aromatic).

A.7.7 Synthesis of $\text{C}_{62}\text{H}_{68}\text{N}_2\text{O}_2\text{Fe}_2$ (**L27**)

To a round bottom flask was added **32** (1.5 g, 1.57 mmol), formaldehyde (1.8 mL, 3.15 mmol), acetonitrile (17 mL), and acetic acid (3 mL). The reaction was stirred for 1 h then the solvent was removed under reduced

pressure. The resulting solid was dissolved in 50:50 THF: MeOH (60 mL) and stirred overnight. The solvent was removed under reduced pressure, extracted with DCM, washed with water, dried with NaSO₄, and filtered to yield **L27** as an orange solid (0.758g, 0.77 mmol, 49%). ¹H NMR (CDCl₃), δ, ppm: 1.77 (s, 12H, Ad), 2.11 (s, 18H, Ad), 2.27 (s, 6H, NCH₃), 2.60 (s, 4H, NCH₂), 3.60 (s, 4H, CH₂), 4.20 (t, 4H, Cp), 4.25 (s, 10H, Cp), 4.47 (t, 4H, Cp), 6.99 (d, 2H, aromatic), 7.36 (d, 2H, aromatic).

Appendix B – Progress Toward an Asymmetric, Salan-Type Redox-Active Ligand

B.1 Introduction

Redox-switchable catalysis offers a method by which the activity and selectivity of a catalyst can be modulated through the oxidation and reduction of either the redox-active ligand or the active metal center.⁸⁸ In 2006, the first redox-switchable catalyst for the ROP of cyclic esters was developed by Gibson, N. Long, and colleagues a salen-type catalyst with a Ti active center and two redox-active ferrocenyl moieties (**1**).⁹⁰ Catalyst **1** was shown to be 30x more active in the native (Fe(II)) state than in the oxidized (Fe(III)) state, which was hypothesized to be due to a change in the electron density at the metal center upon oxidation and reduction. Since this seminal report, a myriad of redox-active ROP catalysts have been developed for the formation of polymers with advanced architectures, such as block copolymers and to study how systematic changes to the ligand scaffold affect the catalytic activity, selectivity, and redox-switchability of these catalysts.²⁴⁹

The Long group has led the efforts in this field to study how systematic changes to the ligand scaffold of these redox-active ROP catalysts affect their catalytic activity, selectivity, and redox-switchability. Through our efforts the effects of the proximity of the redox-active moiety (**2**),⁹¹ the number of redox-active moieties and ligand denticity (**10**, Chapter 2),⁹⁸ ligand connectivity, conjugation (**1z**, **12Ti**, and **12z**, Chapter 3), and metal center identity (Chapter 2 and 3)⁹⁸ on catalytic behavior have been investigated. To further our investigation into these redox-active ROP catalysts we want to investigate how the number of redox-active moieties on a salen-type ligand affect catalytic behavior with the development of **33** (**Figure B.1**). In our previous investigation into the effect of the number of redox-active moieties the comparison was made between a tetradentate catalyst with two ferrocenyl moieties (**1**) and a tridentate catalyst with one ferrocenyl moiety (**10**) it was found that both the catalytic activity and stability may be affected.⁹⁸ However, it is not clear whether these differences are due to the number of redox-active moieties, the ligand denticity or a combination of the two. Therefore, to avoid this uncertainty we propose a study to compare the activity, selectivity, and redox-switchability of **12**, a tetradentate [ONNO] salen with two ferrocenyl moieties, to that of **33**, a tetradentate [ONNO] salen with only 1 ferrocenyl moiety. Herein, the synthesis of **L33** will be described (**Scheme B.1**).

B.2 Results and Discussion

Towards this goal, ligand **L33** was developed as shown in **Scheme B.1**. First ethynylferrocene¹⁶² (**35**) and 3-tert-butyl-5-iodo-2-hydroxybenzaldehyde¹⁶³ (**36**) were obtained from acetylferrocene and 3-tert-butyl-2-hydroxybenzaldehyde, respectively, following literature procedures. Once obtained **35** and **36**, were coupled via Sonogashira coupling using Pd(PPh₃)₂Cl₂, CuCl, and Hunig's base in THF to yield **37**.⁹⁰ Compound **37** was then condensed onto N,N'-dimethylethylenediamine in MeOH followed by reduction with NaBH₄ to yield **38**.²³³ Then, **34**, obtained from 2,4-di-tert-butylphenol with paraformaldehyde, acetic acid, and HBr, was substituted onto **47** with TEA in THF to yield **L33**.

B.3 Conclusion

In this section, a tetradentate [ONNO] salen-type ligand with one ferrocenyl moiety was synthesized for the potential use in the ROP of cyclic esters. This ligand can be metallated with a group IV alkoxide, such as Ti(OⁱPr)₄ or Zr(OⁱBu)₄, then utilized for the polymerization of L-LA or CL at elevated temperatures. The catalytic activity and redox-switchability of these catalyst(s) can then be compared to that seen for the analogous tetradentate [ONNO] salen-type catalysts with two ferrocenyl moieties, **12** to examine the effect that the number

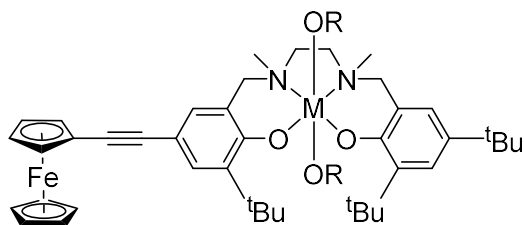
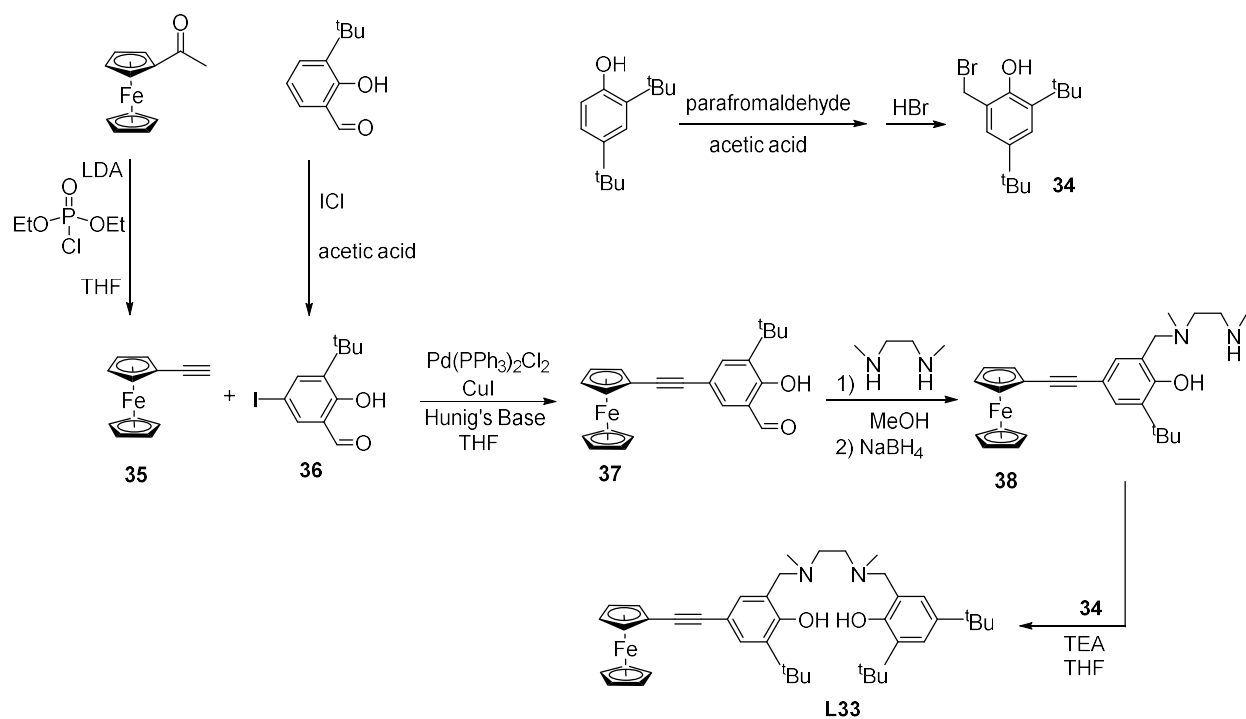


Figure B.1 Redox-active ROP catalyst **33**.

Scheme B.1 Synthesis of [ONNO]-type ligand **L33**



of ferrocenyl moieties has on catalytic activity, selectivity, and redox-switchability. Unlike our previous studies to examine how the number of ferrocenyl moieties affects catalytic activity and redox-switchability this system will allow us to probe this effect without changing the denticity, which has previously been shown to potentially affect catalyst stability as well (**10Ti**, Chapter 2). The development of this ligand will offer further fundamental insight into how ligand structure affects catalytic activity, selectivity, and redox-switchability in order to aid in the systematic development of redox-active ROP catalysts for the synthesis of tailorable polyesters.

B.4 Experimental

B.4.1 General Methods and Materials

THF and methanol were purified using a two-column purification system and degassed *via* freeze-pump-thaw (x3). All NMR solvents were purchased from Cambridge Isotope Laboratories. ¹H NMR spectra were recorded on a Varian 300 MHz spectrometer. Chemical shifts are reported with respect to solvent residual peak, 7.26 (CDCl₃). Acetylferrocene was purchased from Fisher Scientific and purified by silica gel plug using 90:10 hexanes: ethyl acetate as an eluent prior to use. All other reagents were used as received.

B.4.2 Synthesis of Ethynylferrocene (**35**)

To a Schlenk flask was added acetylferrocene (5.0 g, 21.9 mmol) and THF (50 mL) then cooled to -78 °C. Lithium diisopropylamide (LDA) solution (2 M, 33 mmol) was added dropwise via syringe. The solution was stirred for 1 h followed by the addition of diethyl chlorophosphite (3.3 mL, 23.0 mmol) via syringe and stirred for 1 h. The reaction was then warmed to room temperature and stirred for 2 h. The reaction was cooled to -78 °C and LDA (50 mmol) was added dropwise via syringe and stirred 1 h. The reaction was then warmed to room temperature and stirred for 2 h. The reaction was quenched with water (50 mL), extracted with DCM, washed with water, dried with NaSO₄, and filtered. The crude material was purified via silica gel flash column chromatography using 90:10 hexanes: ethyl acetate as an eluent to yield **35** as dark red crystals (3.08 g, 14.7 mmol, 67%). All characterization matched previously reported literature.¹⁶²

B.4.3 Synthesis of 3-tert-butyl-5-iodo-2-hydroxybenzaldehyde (**36**)

To a solution of 3-tert-butyl-2-hydroxybenzaldehyde (5.0 mL, 29.2 mmol) in acetic acid (30 mL) was added ICl (2.05 mL, 40.88 mmol). The mixture was refluxed for 3 h, cooled to room temperature, and quenched with water (50 mL). The organic layer was extracted with DCM, washed with saturated sodium thiosulfate, dried with NaSO₄, and filtered. The crude material was purified via silica gel flash column chromatography using 90:10 hexanes: ethyl acetate as an eluent to yield **36** as a pale-yellow solid (5.47 g, 18.0 mmol, 64%). All characterization matched previously reported literature.¹⁶³

B.4.4 Synthesis of 3-tert-butyl-5-ethynylferrocene-2-hydroxybenzaldehyde (**37**)

To a Schlenk flask was added **35** (3.22 g, 15.35 mmol), **36** (4.24 g, 13.95 mmol), and THF (50 mL). In a glove box, PdCl₂(PPh₃)₂ (0.979 g, 1.395 mmol) and CuI (0.0664 g, 0.348 mmol) were added to a second Schlenk flask. The mixture of **35** and **36** was added to the flask containing [Pd] via cannula. Diisopropylethylamine (4.9 mL, 27.9 mmol) was added via syringe and the solution was stirred at room temperature for 36 h. The solvent was removed under reduced pressure and the crude product was purified via celite/silica gel plug using a gradient eluent

system (100 hexanes to 90:10 hexanes: DCM to 80:20 hexanes: DCM) to yield **37** as an orange solid (3.5 g, 9.07 mmol, 65%). All characterization matched previously reported literature.⁹⁰

B.4.5 Synthesis of 2-(bromomethyl)-4,6-di-tert-butylphenol (**34**)

To a Schlenk flask was added 2,4-di-tert-butylphenol (5.0 g, 24.23 mmol), paraformaldehyde (0.815 g, 26.90 mmol), and acetic acid (15 mL). The reaction was stirred for 2 h followed by the addition of HBr (12.8 mL, 73.17 mmol) dropwise via syringe and the solution was stirred for 30 min. All volatiles were removed under reduced pressure and the resulting oil was stored at -30 °C until orange crystals formed. The solid was filtered, washed with diethyl ether, and dried under vacuum to yield **34** (5.8 g, 19.4 mmol, 80%). All characterization matched previously reported literature.²⁵⁰

B.4.6 Synthesis of $C_{27}H_{34}N_2OFe$ (**38**)

To a Schlenk flask was added **37** (0.250 g, 0.647 mmol) and methanol (10 mL). To a second Schlenk flask was added methanol (5 mL) and N,N'-di-methylethylenediamine (0.08 mL, 0.78 mmol). The diamine solution was added to the solution of **37** dropwise via cannula then stirred for 2.5 h. Sodium borohydride (0.050 g, 1.3 mmol) was then added and the reaction was stirred for 1 h. A second portion of sodium borohydride (0.050 g, 1.3 mmol) and ice-cold water (3 mL) was then added and the reaction was stirred for 2 h. The resulting orange solid was collected via filtration and purified via silica gel plug with 50:48:2 hexanes: DCM: MeOH as an eluent to yield **38** as an orange solid (0.249 g, 0.54 mmol, 84 %). ¹H NMR (CDCl₃), δ , ppm: 1.41 (s, 9H, CCH₃), 2.33 (s, 3H CH₃), 2.42 (s, 3H, CH₃), 2.62 (t, 2H, CH₂), 2.79 (t, 2H, CH₂), 3.68 (s, 2H, CH₂), 4.20 (t, 2H, Cp), 4.24 (s, 5H, Cp), 4.47 (t, 2H, Cp), 7.01 (d, 1H, aromatic), 7.33 (d, 1H, aromatic).

B.4.7 Synthesis of $C_{42}H_{56}N_2O_2Fe$ (**L33**)

To a Schlenk flask was added **38** (0.200 g, 0.436 mmol) and THF (15 mL). To a second Schlenk flask was added **34** (0.130 g, 0.436 mmol) and THF (15 mL). The **38** solution was added to the **34** solution via cannula, then triethylamine (0.7 mL, 0.479 mmol) was added via syringe, and the reaction was stirred for 2 h. The resulting suspension was filtered to remove the white solid, dissolved in DCM, washed with brine, dried with NaSO₄, and filtered. The crude product was triturated from MeOH to yield **L33** as an orange solid (0.159 g, 0.23 mmol, 52%). ¹H NMR (CDCl₃), δ , ppm: 1.28 (s, 9H, CCH₃), 1.41 (s, 18H, CCH₃), 2.26 (s, 6H, CH₃), 2.63 (s, 4H, CH₂), 3.67 (s, 4H, CH₂), 4.21 (t, 2H, Cp), 4.25 (s, 5H, Cp), 4.47 (t, 2H, Cp), 6.80 (d, 1H, aromatic), 7.01 (d, 1H, aromatic), 7.22 (d, 1H, aromatic), 7.33 (d, 1H, aromatic).

Appendix C – Mechanochemically Generated Catalysts for the Polymerization of Methyl Methacrylate and Isoprene

The work discussed in this appendix was originally published by Ross F. Koby, Alicia M. Doerr, Nicholas R. Rightmire, Nathan D. Schley, William W. Brennessel, Brian K. Long, and Timothy P. Hanusa in two peer-reviewed manuscripts:

Ross F. Koby, Alicia M. Doerr, Nicholas R. Rightmire, Nathan D. Schley, Brian K. Long, and Timothy P. Hanusa. "An η^3 -Bound Allyl Ligand on Magnesium in a Mechanochemically Generated Mg/K Allyl Complex." *Angew. Chem. Int. Ed.* **2020**, *59*, 9542-9548, DOI: 10.1002/anie.201916410.

Ross F. Koby, Alicia M. Doerr, Nicholas R. Rightmire, Nathan D. Schley, William W. Brennessel, Brian K. Long, and Timothy P. Hanusa. "Transformations and Catalytic Behavior of a Mechanochemically Generated Dimorphic Organcalcate." *Accepted*.

Ross Koby performed the catalyst synthesis and characterization and performed the majority of the computational work presented within these works, as well as writing the majority of the manuscripts. I performed all polymerizations and polymer characterization. Nicholas Rightmire aided in the synthesis and characterization of the catalysts. Nathan Schley and William Brennessel performed all X-ray crystallography collection and solving of crystal structures. Dr. Brian Long and Dr. Timothy Hanusa advised this work.

C.1 Introduction

S-block metal organometallic compounds such as Grignard reagents and alkyllithiums have revolutionized synthetic organic chemistry since their development in around 1900 and 1917, respectively. However, though many advancements have been made to address the limited covalency and metal-centered redox chemistry of Group II compounds,²⁵¹⁻²⁵⁴ the most direct way to utilize these compounds while working within the electronic configuration constraints of s-block compounds is through ligand development. One ligand design of particular interest is the allyl anion as it can be readily substituted to modify the steric and electronic contributions as well as the complex's solubility and thermal stability.^{255, 256} The allyl anion and its derivatives also exhibit a large range of bonding modes that are accompanied by changes in π -electron delocalization.²⁵⁷ Due to these promising properties, the Hanusa group was interested in the development of a Mg-allyl complex (MgA'_2 , where $\text{A}' = [1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$). However, when synthesized via traditional solution-based methods the THF solvated complex, $[\text{MgA}'_2(\text{thf})_2]$, was found to be the major product and was shown to be inactive for the polymerization of methyl methacrylate (MMA).²⁵⁸ It was hypothesized that this inactivity was due to the solvent coordinating strongly to the metal center inhibiting coordination of MMA, in fact the strength of the Mg-thf interaction prevents the complex from being directly desolvated under high vacuum.²⁵⁹

To further expand these complexes, the Hanusa group is interested in the development of other s-block metal complexes, such as organocalcium complexes, as it has been shown that Ca, Sr, and Ba complexes all exhibit significantly different chemistry than that of their magnesium analogues.^{260, 261} However, when the synthesis of CaA'_2 was attempted via traditional solution-based methods it was again found that the THF solvated complex, $[\text{CaA}'_2(\text{thf})_2]$, was the major product and it was again found that the strength of the Ca-thf interaction prevents the complex from being directly desolvated under high vacuum.^{258, 259} Unlike the Mg-allyl analog, $[\text{CaA}'_2(\text{thf})_2]$ has been shown to be polymerization active,²⁵⁸ however, since coordination of solvent to the metal center can compete

with and even inhibit monomer coordination it can be reasonably postulated that the unsolvated Ca complex, $[\text{CaA}'_2]$ would exhibit greater polymerization activity.

One way to avoid the problems associated with strongly coordinating solvents is to eliminate the use of solvents entirely through mechanochemistry. Mechanochemistry is a powerful synthetic methodology that has been utilized within inorganic, organic, and polymer synthesis to access complexes that are difficult or impossible to obtain otherwise.^{249, 262-265} During mechanochemical syntheses reactions are activated by the absorption of mechanical energy that is generated by compression, stretching, shearing, friction, or acoustic cavitation.²⁶⁶ Due to the power that this method offers to obtain unsolvated complexes the Hanusa group has attempted the synthesis of $[\text{MgA}'_2]$ and $[\text{CaA}'_2]$ utilizing a ball milling process starting from the parent $\text{K}[\text{A}']$ complex and MgX_2 or CaI_2 , respectively. However, unexpectedly it was found that the major product of these reactions were the K/Mg or K/Ca multi-metallic complexes $[\text{K}_2\text{MgA}'_4]$ and $[\text{KCaa}'_3]$, respectively. Utilizing both experimental and computational methods the Hanusa group examined the unique coordination mode and properties of these complexes.^{267, 268} Following their formation we were interested in examining the polymerization activity of these unique complexes. Therefore, we tested the activity of $[\text{K}_2\text{MgA}'_4]$ for the polymerization of MMA as compared to the unsolvated $[(\text{MgA}'_2)_2]$ complex and the parent $\text{K}[\text{A}']$. We also investigated the activity of $[\text{KCaa}'_3]$ for the polymerization of MMA and isoprene at various temperatures.

C.2 Results and Discussion

C.2.1 Polymerization of Methyl Methacrylate using Mg/K Allyl Complexes

Metal (trimethylsilyl)allyl complexes have been previously evaluated as initiators for the polymerization of MMA.^{258, 269-271} Consequently, the MMA polymerization activity of the $[\text{K}_2\text{MgA}'_4]$ was evaluated and compared to the activities of the $[(\text{MgA}'_2)_2]$ complex and the previously reported $\text{K}[\text{A}']$.²⁷⁰ All polymerizations were conducted under an inert atmosphere in which the initiator, MMA (0.5 g), and toluene (2 M) were combined and allowed to react at the designated temperature and time, as detailed in **Table C.1**. Room-temperature polymerizations using $\text{K}[\text{A}']$, $[\text{K}_2\text{MgA}'_4]$, and $[(\text{MgA}'_2)_2]$ and a high monomer/ initiator loading (100:1) were found to reach 94%, 72%, and 19% yield, respectively, in 24 h (**Table C.1**, entries 1-3). These results are consistent with the hypothesis that the polymerization inactivity of previously reported $[\text{MgA}'_2(\text{thf})_2]$ species is due in part to solvent coordination thereby hindering monomer coordination to the metal center.²⁵⁸

When comparing the polymers produced using $\text{K}[\text{A}']$, $[\text{K}_2\text{MgA}'_4]$, and $[(\text{MgA}'_2)_2]$, we found that $\text{K}[\text{A}']$ and $[\text{K}_2\text{MgA}'_4]$ both produce atactic poly(methyl methacrylate) (PMMA) with similar molecular weights (M_n) and dispersities ($\mathcal{D}$). In contrast, $[(\text{MgA}'_2)_2]$ produced isotactically enriched PMMA having significantly higher M_n and a broader dispersity ($\mathcal{D} = 3.83$; **Table C.1**, entry 3). To further investigate the activity of $[\text{K}_2\text{MgA}'_4]$, MMA polymerizations were conducted at lower initiator loading (250:1) and shorter polymerization time (1 h). Again, $\text{K}[\text{A}']$ and $[\text{K}_2\text{MgA}'_4]$ exhibited similar activities reaching 90% and 72% yield, respectively (**Table C.1**, entries 4, 5), indicating that polymerizations using these initiators are rapid and reaching their maximum possible conversion in ≤ 1 h. However, $[(\text{MgA}'_2)_2]$ exhibited dramatically decreased activity, only producing trace amounts of polymer under identical conditions (**Table C.1**, entry 6).

Lastly, the catalytic activity of $[\text{K}_2\text{MgA}'_4]$ was examined for MMA polymerizations at 0 °C and a further decreased initiator loading of 1000:1 (MMA: $[\text{K}_2\text{MgA}'_4]$). $\text{K}[\text{A}']$ again exhibited similar activity reaching 92% in 1 h (**Table C.1**, entry 7), whereas $[\text{K}_2\text{MgA}'_4]$ exhibited an increase in activity at this lower polymerization

Table C.1 Polymerization of MMA with initiator K[A'], [K₂MgA'₄], and [(MgA'₂)₂].^a

Entry	Initiator	Mono/Init	T (°C)	t (h)	Yield ^b (%)	M _n ^c (gmol ⁻¹)	<i>D</i>	Tacticity ^d
1	K[A']	100:1	RT	24	94	19,100	2.68	26/50/24
2	[K ₂ MgA' ₄]	100:1	RT	24	72	17,800	2.76	25/52/23
3	[(MgA' ₂) ₂]	100:1	RT	24	19	113,400	3.83	71/16/12
4	K[A']	250:1	RT	1	90	25,500	2.37	-----
5	[K ₂ MgA' ₄]	250:1	RT	1	72	20,500	2.18	-----
6	[(MgA' ₂) ₂]	250:1	RT	1	trace	-----	-----	-----
7	K[A']	1000:1	0	1	92	46,900	2.62	-----
8	[K ₂ MgA' ₄]	1000:1	0	1	89	27,800	2.89	-----
9	[(MgA' ₂) ₂]	1000:1	0	1	0	-----	-----	-----

^aGeneral conditions: 0.5 g monomer, 2 M in toluene, quenched with MeOH. ^bYield was determined based upon isolated polymer mass and initial mass of MMA. ^cDetermined using GPC at 40 °C in THF and are reported relative to PMMA standards. ^dTacticities are reported as percent mm/mr/rr triads as determined from ¹H NMR spectra.

temperature, ultimately reaching 89% conversion in 1 h (**Table C.1**, entry 8). Though the source of this increase in activity is not yet fully understood, we hypothesize that this may indicate that $[\text{K}_2\text{MgA}'_4]$ undergoes decomposition and/or deactivation at room temperature, which is slowed or suppressed at temperatures at or below 0 °C.²⁷²⁻²⁷⁵ Finally, and as expected at this point, $[(\text{MgA}'_2)_2]$ exhibited no polymerization activity under these conditions (**Table C.1**, entry 9).

C.2.2 Polymerization of Methyl Methacrylate and Isoprene using Ca/K Allyl Complexes

Due to our previous success testing metal (trimethylsilyl)allyl complexes ($\text{K}[\text{A}']$, $[(\text{MgA}'_2)_2]$, and $[\text{K}_2\text{MgA}'_4]$, Appendix B.2.1) for the polymerization of MMA, the polymerization activity of $[\text{KCaA}'_3]$ was also evaluated for the polymerization of MMA at a variety of temperatures. All polymerizations were conducted under an inert atmosphere in which the initiator, MMA (0.25 g), and toluene (0.5 M) were combined and allowed to react at the designated temperature (RT, 0 °C, and -78 °C) for 8 min then analyzed to determine the polymer yield, turn over frequency (TOF), molecular weight, dispersity, and polymer tacticity (**Table C.2**, entry 1-3). $[\text{KCaA}'_3]$ was found to be polymerization active at all three temperatures reaching 22, 49, and 23% yield and TOFs of 27, 61, and 29 min⁻¹ at RT, 0 °C, and -78 °C, respectively. It was hypothesized that the increase in TOF observed when conducting the polymerization at 0 °C instead of room temperature could be the result of either the suppression of “backbiting” cyclization reactions or the suppression of possible initiator degradation.^{272, 275}

Regardless of polymerization temperature $[\text{KCaA}'_3]$ was found to produce PMMA with molecular weights between 63,600-76,300 g/mol and high dispersities ($D = 8.25\text{-}10.4$). These high dispersities were similar to the results obtained using a Grignard reagent as an initiator for the polymerization of MMA (**Table C.2**, entry 4).²⁷⁶ Grignard's are found to result in high dispersities because they are subject to Schlenk equilibria ($2 \text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$) which leads to the presence of multiple active sites and the likely presence of side reactions, both of which can complicate the polymerization. Based on the modeling and computational data gathered by our collaborators,²⁶⁸ it is reasonable that some Schlenk-type rearrangements may occur resulting in the generation of multiple functional species in solutions of $[\text{KCaA}'_3]$ (i.e.: $[\text{KCaA}'_3] \rightleftharpoons \text{K}[\text{A}'] + [\text{CaA}'_2]$), contributing to the broad dispersities observed. Lastly, $[\text{KCaA}'_3]$ was found to generate isotactically enriched PMMA (72-74% isotacticity depending on polymerization temperature whereas the parent complex $\text{K}[\text{A}']$ produces atactic PMMA (**Table C.2**, entry 5).^{267, 270, 277}

While s-block complexes have been utilized as catalysts for the polymerization of alkenes (as previously discussed) the polymerization of dienes with these complexes is much less studied.²⁶⁰ A few examples of using Ca and Ba complexes for the polymerization of butadiene have been reported,^{278, 279} as well as two examples for Ca complexes being used for the polymerization of isoprene.²⁸⁰ While the polymerization of isoprene can lead to more complex stereo- and regiochemistry than the polymerization of butadiene, isoprene is easier to work with as it exists as a liquid at room temperature as compared to butadiene which is a gas. Therefore, we chose to utilize isoprene to study the activity of $[\text{KCaA}'_3]$, the parent complex ($\text{K}[\text{A}']$), and the solvated Ca complex ($[\text{CaA}'_2(\text{thf})_2]$) towards the polymerization of a diene. All polymerizations were conducted under an inert atmosphere in which the initiator, isoprene (0.25 g), and toluene (4 mL) were combined and allowed to react at the designated temperature (RT, 50 °C, and 80 °C) for 12 hours then analyzed to determine the polymer yield, molecular weight, dispersity, and polymer regiochemistry (**Table C.3**, entry 1-7). The parent $\text{K}[\text{A}']$ complex, $[\text{CaA}'_2(\text{thf})_2]$, and a combination of both $\text{K}[\text{A}']$ plus $[\text{CaA}'_2(\text{thf})_2]$ were all found to be inactive for the

Table C.2 Polymerization of MMA.

Entry	Initiator	Mono /cat	T (°C)	t	Yield (%)	TOF (min ⁻¹)	M _n (g/mol)	<i>Đ</i>	Tacticity ^c	Ref.
1	[KC <i>CaA'</i> ₃] ^a	1000:1	RT	8 min	22	27	63,600 ^b	8.44 ^b	69/22/9	this work
2	[KC <i>CaA'</i> ₃] ^a	1000:1	0	8 min	49	61	75,700 ^b	8.25 ^b	64/25/11	this work
3	[KC <i>CaA'</i> ₃] ^a	1000:1	-78	8 min	23	29	76,300 ^b	10.4 ^b	66/28/6	this work
4	(ⁿ Bu)MgBr	50:1	-78	72 h	14	---	7,420	11.2	21/15/64	²⁷⁶
5	K[A']	1000:1	-78	30 s	87	1150	---	---	25/53/22	²⁷⁷

^aPolymerization Conditions: 0.25 g monomer, 0.5 M with respect to monomer in toluene, cooled to the respective temperature before monomer addition, then quenched with acidic MeOH and precipitated into MeOH. ^bNumber average molecular weights (M_n) and dispersities (*Đ*) were measured via GPC at 40 °C in THF and are reported relative to PMMA standards. ^cTacticities are reported as percent mm/mr/rr triads as determined from ¹H NMR spectra.

Table C.3 Polymerization of Isoprene.

Entry	Initiator	Mono /cat	T (°C)	t (h)	Yield (%)	M _n (g/mol)	<i>Đ</i>	1,2/1,4/3,4	Ref.
1	[KC <i>CaA'</i> ₃] ^a	200:1	RT	12	98	16,300 ^b	1.27 ^b	0/63/37 ^c	this work
2	[KC <i>CaA'</i> ₃] ^a	200:1	50	12	99	14,200	1.52 ^b	0/64/36 ^c	this work
3	[KC <i>CaA'</i> ₃] ^a	200:1	80	12	98	11,400	1.63 ^b	0/64/36 ^c	this work
4	[KC <i>CaA'</i> ₃] + 1 Eq THF ^a	200:1	RT	12	0	---	---	---	this work
5	K[A'] ^a	200:1	RT	12	0	---	---	---	this work
6	[CaA' ₂ (thf) ₂] ^a	200:1	RT	12	0	---	---	---	this work
7	K[A'] + [CaA' ₂ (thf) ₂] ^a	200: 200:1	RT	12	0	---	---	---	this work
8	<i>Sec</i> -BuLi		80	2	---	39,300	1.04	---	²⁸⁰
9	(DMAT) ₂ Ca·(thf) ₂	100:1	50	1	---	20,600	1.30	22/52/26	²⁸⁰
10	[(DMAT)(9-TMS-FI)Ca] ₂	100:1	50	0.2 5	---	15,400	1.26	11/52/37	²⁸⁰

^aPolymerization Conditions: 0.25 g monomer, 4 mL toluene, quenched with acidic MeOH and precipitated into MeOH. ^bNumber average molecular weight (M_n) and dispersities (*Đ*) were measured via GPC at 30 °C in THF using triple detection. ^cRegiochemistry determined via ¹H NMR spectra.

polymerization of isoprene. Conversely, $[\text{KCaA}'_3]$ was found to be polymerization active at all three temperatures tested (RT, 50 °C, and 80 °C). At all temperatures, the polymerization was found to reach 98-99 % conversion within 12 h producing polyisoprene with molecular weights between 11,400-16,300 g/mol and low to moderate dispersities ($\bar{D} > 1.63$). It was also found that at all temperatures the polyisoprene produced by $[\text{KCaA}'_3]$ was enriched with the 1,4-insertion product over the 3,4-insertion product (64:36 ratio). Lastly, when the polymerization behavior of $[\text{KCaA}'_3]$ in the presence of 1 molar equivalence of THF was probed, the complex was found to be polymerization inactive supporting our hypothesis that solvent coordination to the active metal center may hinder or even inhibit polymerization behavior in these complexes. Furthermore, these results indicate that the polymerization behavior observed for $[\text{KCaA}'_3]$ is the direct result of the unique, solvent free K-Ca complex that can only be obtained via mechanochemical methods.

C.3 Conclusion

Since the development of s-block complexes such as Grignard reagents and alkylolithiums which revolutionized modern synthetic organic chemistry, interest in the further investigation of s-block complexes has persisted. One of the main ways in which these compounds can be tailored is through modification to the ligand scaffold. The allyl anion is of particular interest as a ligand design as it can be readily substituted, and the allyl anion and its derivatives can exhibit a large range of bonding modes as the π -electron delocalization of the ligand changes. Due to these properties the Hanusa group was interested in developing a Mg- and a Ca-allyl complex ($[\text{MaA}'_2]$ and $[\text{CaA}'_2]$, respectively, where $\text{A}' = [1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]$). However, when traditional solution-based synthetic methods were used the major product of the reactions were the solvated complexes $[\text{MgA}'_2(\text{thf})_2]$ and $[\text{CaA}'_2(\text{thf})_2]$ wherein the strength of the M-thf interaction prevented the complex from being directly desolvated under high vacuum. When tested for the polymerization of MMA $[\text{MgA}'_2(\text{thf})_2]$ was found to be inactive which was hypothesized to be due to the strength of the thf coordination inhibiting monomer coordination. Therefore, a solventless method of synthesis such as mechanochemistry is a highly attractive method by which the desired unsolvated complexes may be obtained. However, when the Mg- and Ca-allyl complexes were synthesized via mechanochemistry using a ball milling process starting from $\text{K}[\text{A}']$ and MgX_2 or CaI_2 multi-metallic complexes $[\text{K}_2\text{MgA}'_4]$ and $[\text{KCaA}'_3]$, respectively, were obtained instead of the desired monometallic complexes. Upon formation of these unique complexes, we wanted to probe their activity for the polymerization of MMA and isoprene.

First, the activity of $[\text{K}_2\text{MgA}'_4]$ was tested for the polymerization of MMA at both room temperature and 0 °C and the activity and tacticity of the polymer produced were compared to that of the parent $\text{K}[\text{A}']$ complex and the unsolvated $[(\text{MgA}'_2)_2]$ complex. It was found that $[\text{K}_2\text{MgA}'_4]$ was only slightly less active than $\text{K}[\text{A}']$ but significantly more active than $[(\text{MgA}'_2)_2]$ at both temperatures, producing with molecular weights between 17,800-27,800 g/mol and moderate dispersities ($\bar{D} = 2.18\text{-}2.89$). It was also shown that while $[(\text{MgA}'_2)_2]$ produced isotactically enriched PMMA both $\text{K}[\text{A}']$ and $[\text{K}_2\text{MgA}'_4]$ produced atactic PMMA. Next, $[\text{KCaA}'_3]$ was found to be active for the polymerization of MMA at RT, 0 °C, and -78 °C producing PMMA with molecular weights between 63,600-76,300 g/mol and high dispersities ($\bar{D} = 8.25\text{-}10.4$). $[\text{KCaA}'_3]$ was also found to be active for the polymerization of isoprene at RT, 50 °C, and 80 °C producing polyisoprene with molecular weights between 11,400-16,300 g/mol and low to moderate dispersities ($\bar{D} > 1.63$). Conversely, the parent $\text{K}[\text{A}']$ complex and $[\text{CaA}'_2(\text{thf})_2]$ were both found to be inactive for the polymerization of isoprene. All of these results support our

hypothesis that that solvent coordination to these complexes active metal center may hinder or even inhibit polymerization behavior. Furthermore, we have demonstrated that mechanochemistry can be used to obtain unique multi-metallic complexes that cannot be obtained via traditional solution-based synthetic methods and that these multi-metallic complexes are active for the polymerization of MMA and isoprene and may be used to produce PMMA and/or polyisoprene that cannot be obtained with either their unimetallic analogues.

C.4 Experimental

C.4.1 General Methods and Materials

Molecular weights (M_n) of polymethylmethacrylate were determined using a Tosoh EcoSec GPC at 40 °C in THF and referenced to polymethylmethacrylate standards. Molecular weights (M_n) of polyisoprene were determined using a Malvern Omisec system using triple detection and three Viscotek styrene divinylbenzene copolymer columns (in series T3000, T4000, and T5000) at a flow rate of 1 mL min⁻¹ and thermostatted to 30 °C with THF as the eluent. ¹H NMR of polymers were recorded on a Varian 300 spectrometer and chemical shifts are reported with respect to solvent residual peaks, i.e., δ 7.26 ppm (CDCl₃, purchased from Cambridge Isotope Laboratories). Methyl methacrylate was purchased from Acros, run through a basic alumina column, dried over 4Å sieves, vacuum transferred, and then degassed via three freeze-pump-thaw cycles. Isoprene was purchased from Acros, distilled off CaH₂, and degassed via three freeze-pump-thaw cycles.

C.4.2 General MMA Polymerization Conditions using Mg/K Complexes

Under an inert atmosphere, MMA (0.5 g, 5 mmol) was added to a solution of catalyst (50, 20, or 5 μ mol) in toluene (2.5 mL). The polymerization was held at the designated temperature and stirred continuously for the time prescribed. The polymerization was quenched via exposure to air and the polymer precipitated via dropwise addition to MeOH. The resultant polymer was isolated via filtration then re-dissolved in CH₂Cl₂, re-precipitated into MeOH, filtered, and dried. Polymer tacticity was determined with ¹H NMR in CDCl₃.^{281, 282}

C.4.3 General MMA Polymerization Conditions using Ca/K Complexes

Under an inert atmosphere, MMA (0.25 g, 2.5 mmol) was added to a solution of K[CaA'₃] (2.5 μ mol) in toluene (5 mL) cooled to the designated temperature. The polymerization was held at the designated temperature and stirred continuously for 8 min. The polymerization was quenched with acidic methanol (3 mL) and the polymer precipitated via dropwise addition to MeOH. The resultant polymer was isolated via filtration and dried. Polymer tacticity was determined with ¹H NMR in CDCl₃.^{281, 282}

C.4.4 General Isoprene Polymerization Conditions using Ca/K Complexes

Under an inert atmosphere, isoprene (0.25 g, 3.67 mmol) was added to a solution of K[CaA'₃] (11.7 mg, 0.0184 mmol) in toluene (4 mL) at the designated temperature. The polymerization was stirred continuously for 12 h at the designated temperature. The polymerization was quenched with acidic methanol (3 mL) and the polymer precipitated via dropwise addition to MeOH. The methanol was decanted off then the polymer was dried. Polymer regiochemistry was determined with ¹H NMR in CDCl₃.²⁸³⁻²⁸⁵

Vita

Alicia Marie Doerr was born and raised in Stillwater, Minnesota. After graduating high school in 2012, she began her undergraduate career at the University of Minnesota-Morris (UMM) in Morris, MN where she earned her Bachelor of Arts in chemistry and a minor in mathematics in 2016. During her time at UMM, Alicia did undergraduate research under Professor Nancy Carpenter. She was also a member of the Women's Track and Field team as well as being co-captain during her senior year. After graduation, Alicia started her graduate studies at the University of Tennessee-Knoxville (UTK). Alicia worked for Dr. Brian K. Long and during her time at UTK she published multiple manuscripts and had the opportunity to present her work during departmental seminars and at the Excellence in Graduate Polymer Research Symposium at the ACS National Meeting in April 2021.